

**Sorption of hydrophobic organic compounds (HOCs)  
to inorganic surfaces in aqueous solutions**

**Dissertation**

zur Erlangung des akademischen Grades eines  
Doktors der Naturwissenschaften  
– Dr. rer. nat. –

der Fakultät für Chemie  
der Universität Duisburg-Essen

vorgelegt von  
Yuan Qian  
aus Jiangsu, V. R. China

**2010**

Tag der Disputation: 27.01.2011

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## **Acknowledgements**

I am heartily thankful to my supervisor Prof. Torsten C. Schmidt for the continuous support, guidance, and encouragement throughout the work.

Special thanks to Dr. Holger Krohn for the major support on the construct of scanning electrochemical microscopy and the knowledgeable discussions on the method development. Thanks also to Dr. Erping Bi for the help of column packing and Mrs. Claudia Schenk for the BET surface area determination.

I am deeply grateful to Prof. Dr. Christian Mayer, Prof. Dr. Kai-Uwe Goss and Dr. Satoshi Endo for the helpful suggestions and valuable discussions.

I would also like to acknowledge the contributions of Prof. Dr. Karl Molt and Dr. Maik Jochmann for their valuable comments, Lijun Zhang, Fayaz Kondagula and Alexandra Jarocki for their helpful discussions, Tjorben Posch, Rani Bakkour, and Laura Jung for their lab work assistance.

As well, my gratitude goes to all the members of Instrumental Analytical Chemistry group.

My most heartily thanks go to my wife and my parents for their understanding, love, and encouragement.



## Abstract

Sorption of hydrophobic organic compounds (HOCs) to hydrophilic inorganic surfaces in aqueous systems is an important process, because HOCs are common contaminants and the sorption controls their concentration and rate of transport in the environment. Furthermore, in environmental chemistry and analysis, sorption of HOCs to inorganic surfaces, in particular to untreated (uncoated) glass surfaces, causes the loss of analyte and then confuses subsequent data interpretation. For a better understanding of the process and developing a predictive tool, five selected polycyclic aromatic hydrocarbons (PAHs, naphthalene, fluorene, phenanthrene, anthracene and pyrene) and four pairs of n- and cycloalkanes (C5 to C8) have been used as chemical probes. Their sorption behaviors to different hydrophilic inorganic surfaces (e.g. borosilicate glass, silica gel, aluminum oxide and titanium oxide) were systematically investigated.

From a practical point of view, glassware is the commonly used container in analysis. Therefore, sorption coefficients ( $K_d$ ) of five selected PAHs to the frequently used laboratorial glass surfaces (borosilicate glass) were firstly investigated by using column chromatography. The validation of column method was carried out by comparing the data measured in column chromatography to that obtained in batch experiments. After validation, the influence of environmental factors on  $K_d$ , such as ionic strength, pH value, co-solvent, coated surface and temperature, were comprehensively studied. Our data revealed that (1) mass loss caused by sorption on glass walls strongly depends on the ratio of solution volume to contacted surface area (V/S) and (2) use of cosolvent or silane coated glass surfaces is often not sufficient to suppress sorption for large PAHs.

Based on the successful application of column chromatography in glass surface studies, this method was extended to use in the further investigation of sorption to other mineral surfaces (e.g. silica gel, aluminum oxide and titanium oxide). Sorption coefficients ( $K_d$ ) were determined under different environmental conditions (i.e. ionic strength, pH value and temperature). In particular, the influence of particle size and pore size, which played an important role for the extent of sorption for porous sorbent, was focused on. In this study, the most important observation is that for porous material, not all the N<sub>2</sub>-BET determined surface area was effective for sorption in water-mineral systems.

Generally, a linear relationship between  $\log K_d$  and the corresponding water solubility of the subcooled liquid ( $\log S_w$ ) of the investigated PAHs was found on all investigated inorganic surfaces. It provides a tool to predict sorption behavior of other PAHs to inorganic surfaces. The determined sorption coefficients ( $K_d$ ) at various environmental conditions on all investigated inorganic surfaces showed that the ionic strength, solution pH and temperature had no significant effect on the sorption process, which indicates that nonspecific interactions (such as van der Waal's forces) dominate the sorption process.

Two sorption modes, adsorption and absorption, are currently considered as sorption mechanisms in sorbent-water systems. The ratio of the sorbent-air/sorbent-water distribution coefficients of n-alkanes to that of cycloalkanes with the same number of carbon atoms ( $K_n/K_c$ ) was recently demonstrated to be indicative of the mode of sorption ( $K_n/K_c < 1$  indicates adsorption, while  $\sim 1$  indicates absorption). Following this approach, four pairs of n- and cycloalkanes (C5 to C8) were investigated with regard to sorption to silica and aluminum oxide surfaces by using batch experiments. After calculating the ratio of  $K_n/K_c$  the implications for the sorption mode have been discussed.

To measure in-situ the concentration gradient formed near to inorganic surfaces, a highly spatially resolved electrochemical method, scanning electrochemical microscopy (SECM), was applied. The concentration gradient was represented through an indirect method, measuring the change of conductivity in ionic solutions. The conductivity was observed to decrease significantly with increasing distance between 1 to 300  $\mu\text{m}$ . However, a full explanation of this phenomenon needs further investigations.

## Notation

$C_0$	initial aqueous phase concentration [mg/L]
$C_s$	sorbed phase concentration at equilibrium [mg/kg]
$C_w$	aqueous phase concentration at equilibrium [mg/L]
$K_{aw}$	air-water partitioning coefficient [-]
$K_d$	sorption coefficient [L/kg]
$K_d'$	apparent sorption coefficient [L/kg]
$K_{d,SA}$	surface normalized sorption coefficient [L/m <sup>2</sup> ]
$K_F$	Freundlich sorption coefficient [(mg/kg)/(mg/L) <sup>n</sup> ]
$K_n/K_c$	the ratio of the sorption coefficient of the n-alkane and the cycloalkane [-]
$K_{ow}$	octanol-water distribution coefficient [-]
$n$	Freundlich exponent [-]
$q$	flowrate [mL/min]
$R$	gas constant [8.3145 J/(mol K)]
$R_f$	retardation factor [-]
$S_w$	water solubility [mg/L]
$t$	retention time of target compounds [s]
$t'$	traveling time through the injector and connecting capillary between injector and detector [s]
$t_o$	dead time (or hold-up time, ) of column (i.e., retention time of conservative tracer) [s]
$T$	temperature [K]
$V/S$	the ratio of solution volume to contacted surface area [mL/cm <sup>2</sup> ]
$\Delta H$	enthalpy change [kJ/mol]
$\Delta S$	entropy change [kJ/(mol K)]
$\rho_b$	bulk density [g/cm <sup>3</sup> ]
$\theta$	porosity [-]



# Contents

<b>Acknowledgement .....</b>	<b>.....</b>
<b>Abstract.....</b>	<b>I</b>
<b>Notation.....</b>	<b>III</b>
<b>1 Introduction .....</b>	<b>1</b>
<b>1.1 Background.....</b>	<b>1</b>
<b>1.2 Sorption of hydrophobic organic compounds to inorganic surfaces.....</b>	<b>2</b>
<b>1.3 Methods for measuring sorption coefficient.....</b>	<b>3</b>
1.3.1 Batch approach .....	3
1.3.2 Column chromatography approach .....	4
1.3.3 Principles of column experiment .....	5
<b>1.4 Sorption mechanisms of HOCs to inorganic surfaces .....</b>	<b>7</b>
<b>1.5 Scanning electrochemical microscopy (SECM).....</b>	<b>8</b>
<b>1.6 References .....</b>	<b>9</b>
<b>2 Aims.....</b>	<b>13</b>
<b>3 Sorption of polycyclic aromatic hydrocarbons (PAHs) on glass surfaces.....</b>	<b>15</b>
<b>3.1 Introduction.....</b>	<b>15</b>
<b>3.2 Materials and methods .....</b>	<b>16</b>
3.2.1 Materials.....	16
3.2.2 Methods.....	17
3.2.3 Mass recovery.....	20
<b>3.3 Results and discussion .....</b>	<b>21</b>
3.3.1 Sorption coefficient $K_d$ .....	21
3.3.2 Effect of solution chemistry.....	24
3.3.3 Effect of Temperature.....	26
3.3.4 Effect of surface property.....	27
<b>3.4 Implications .....</b>	<b>28</b>
<b>3.5 Acknowledgements.....</b>	<b>28</b>
<b>3.6 References.....</b>	<b>28</b>

<b>4 Sorption of polycyclic aromatic hydrocarbons (PAHs) on mineral surfaces in aqueous solution: an HPLC type column study.....</b>	<b>33</b>
<b>4.1 Introduction.....</b>	<b>33</b>
<b>4.2 Materials and methods .....</b>	<b>34</b>
4.2.1 Materials.....	34
4.2.2 Method.....	36
4.2.3 Mass recovery.....	37
<b>4.3 Results and discussion .....</b>	<b>37</b>
4.3.1 Sorption coefficient $K_d$ .....	37
4.3.2 Effect of surface characteristics.....	40
4.3.3 Effect of solution chemistry.....	41
4.3.4 Effect of temperature .....	43
<b>4.4 Conclusions .....</b>	<b>45</b>
<b>4.5 Acknowledgements.....</b>	<b>45</b>
<b>4.6 References.....</b>	<b>45</b>
<b>5 Characterizing the sorption mode to mineral surfaces in aqueous solution by using alkane and cycloalkane probe Compounds.....</b>	<b>49</b>
<b>5.1 Introduction.....</b>	<b>49</b>
<b>5.2 Materials and methods .....</b>	<b>51</b>
5.2.1 Materials.....	51
5.2.2 Methods.....	52
<b>5.3 Results and discussion .....</b>	<b>53</b>
5.3.1 Sorption isotherms.....	53
5.3.2 $K_n/K_c$ ratio for sorption to water-mineral surfaces.....	58
<b>5.4 Acknowledgements.....</b>	<b>60</b>
<b>5.5 References.....</b>	<b>60</b>
<b>6 Characterization of sorption mechanism in near-surface zone on hydrophilic surfaces using scanning electrochemical microscopy (SECM).....</b>	<b>63</b>
<b>6.1 Introduction.....</b>	<b>63</b>
<b>6.2 Materials.....</b>	<b>64</b>

<b>6.3 Methods .....</b>	<b>65</b>
6.3.1 Sorption on ITO glass.....	65
6.3.2 Sorption on nonconductive glass.....	66
<b>6.4 Results and discussions.....</b>	<b>67</b>
6.4.1 Sorption on ITO glass.....	67
6.4.2 Sorption on nonconductive glass.....	69
<b>6.5 References.....</b>	<b>72</b>
<b>7 General conclusions and Outlook.....</b>	<b>73</b>
<b>8 Appendixes.....</b>	<b>75</b>



## 1. Introduction

### 1.1 Background

The process in which chemicals become associated with solid phases is generally referred to as sorption. It is *adsorption* if the molecules attach to a two-dimensional surface, while it is *absorption* if the molecules penetrate into a three-dimensional matrix. This phase transfer process may involve vapor molecules or dissolved molecules associating with solid phases. The term sorption is more appropriately used in environmental situations to denote the uptake of a solute by a solid (soil or sediment) without reference to a specific mechanism, or when the mechanism is uncertain (Chiou, 2002, Schwarzenbach et al., 2003).

Sorption is extremely important because it plays a major role in determining the fate and impacts of chemicals in the environment. The environmental transport of waterborne molecules must differ from the movements of the same kind of molecules attached to particles that settle. Also, transport of a given compound in porous media such as soils, sediments, and aquifers is strongly influenced by the compound's tendency to sorb to the various components of the solid matrix (Schwarzenbach et al., 2003). Additionally, sorption affects almost all environmental fate processes including volatilization, bioavailability, biodegradability, photolysis, and hydrolysis (Doucette, 2003).

In solid-water systems, sorption is generally quantified by the sorption coefficient ( $K_d$ ) which describes the extent of solute distribution between solid (e.g., soil, sediment, or aquifer) and aqueous phase. The  $K_d$  is defined as the ratio of its concentration in the solid phase ( $C_s$ ) to its concentration in the aqueous phase ( $C_w$ ) at equilibrium:

$$K_d = C_s / C_w \quad (1-1)$$

If sorption isotherm is linear, the sorption coefficient  $K_d$  is a constant, thus the concentration of the chemical sorbed on solid phase is directly proportional to the concentration of the chemical in water.

For nonlinear sorption, several models are proposed to describe the isotherm, such as Langmuir, BET, Gibbs and Freundlich model. However in water phase related sorption, only the Freundlich model and linear model fit better to the sorption data (Delle Site,

2001). Therefore, Freundlich equation is the most commonly used to describe the relationship between  $C_s$  and  $C_w$  in nonlinear sorption.

$$C_s = K_F C_w^n \quad (1-2)$$

where  $K_F$  is the Freundlich sorption coefficient and  $n$  is the Freundlich exponent. When  $n$  equals one, the Freundlich equation (1-2) simplifies to equation (1-1), and  $K_F$  and  $K_d$  become equivalent.

Many factors can potentially affect the distribution of an organic chemical between an aqueous and solid phase. These include environmental variables such as temperature (ten Hulscher et al., 1996, Piatt et al., 1996), solution pH, ionic strength (Bi et al., 2007, Tang et al., 2010, Li et al., 2010), and dissolved organic matter concentration (Schwarzenbach et al., 1981, Grathwohl, 1990, Bi et al., 2007, Li et al., 2010). The presence of cosolvents (Wood et al., 1990.) also can significantly impact sorption. In addition, factors related specifically to the experimental determination of sorption coefficients such as the solid to solution ratio (Voice et al., 1983) and equilibration time (Chiou et al., 1979, Schwarzenbach et al., 2003) can be relevant.

### **1.2 Sorption of hydrophobic organic compounds to inorganic surfaces**

Hydrophobic organic compounds (HOCs), including aromatic compounds in petroleum and fuel residue, and chlorinated compounds in commercial solvents (Luthy et al., 1997), are common contaminants in environmental matrices. In the environment, sorption of HOCs is dominated by organic matter (OM). However, for solids containing no or low contents of OM (as a rule-of-thumb less than 0.1% (w/w)), sorption to mineral surfaces becomes the dominant process (Chiou et al., 1983, Su et al., 2006).

For HOCs, numerous investigations reported a significant sorption to mineral surfaces in aqueous solutions (Huang et al., 1996, Mader et al., 1997, Hundal et al., 2001, Su et al., 2006, Müller et al., 2007, Wang et al., 2008). Therefore, it is important to understand and be able to predict the transport and fate of HOC to inorganic surfaces.

Furthermore, in environmental chemistry and analysis, sorption of organic compounds to inorganic surfaces, in particular to untreated (uncoated) glass surfaces, is important if the concentrations of the organic compounds under investigation are small. The loss of

analyte due to sorption can confuse subsequent data interpretation, especially for HOCs, which have poor solubility in aqueous solution. Although numerous investigations that focused on the study of HOCs have reported a significant loss of analyte that was subscribed to adsorption to the walls of glass vials (Yang et al., 1998, Ackerman et al., 2000, Hundal et al., 2001, Poerschmann et al., 2000, Xia et al., 2001), in most reports this process was merely held responsible for observed mass losses without a detailed investigation. A systematic investigation of sorption to inorganic surfaces, especially to untreated glass surface, and developing a predictive method that enables a-priori decisions if this process is critical or not, are important issues from the practical side.

### **1.3 Methods for measuring sorption coefficient**

#### **1.3.1 Batch approach**

Sorption coefficients of organic compounds to inorganic sorbents can be determined by batch approach and by dynamic liquid chromatography in columns. Equilibrium sorption isotherms for a given sorbate-sorbent system should be independent of the method of determination.

The conventional method which has been used most often to determine sorption coefficients is the batch method. In batch experiments, a small given amount of the sorbent (i.e., sediment, solid or aquifer) is agitated with a solution containing the chemical of interest. Then, the concentrations in one or both phases are measured as a function of time or once equilibrium is achieved. The  $K_d$  value is then calculated using linear or nonlinear model (see section 1.1).

A batch experiment is conceptually simple but time consuming. Furthermore, it may yield unreliable sorption data, if analytes show weak sorption or poor solubility, such as HOCs, which causes difficulties in precisely detecting the solid-phase concentration or the difference between initial and equilibrium aqueous concentration of the solute (Bi et al., 2006). Furthermore, they are subject to a variety of operational difficulties and experimental artifacts related to the incomplete separation of phases, agitation speed, insufficient time for equilibration, and exposure of new sorptive surfaces during agitation (Doucette, 2003). Consequently, due to the relatively long time required for achieving equilibrium, the additional losses caused by microbial degradation and volatilization can

result in overestimation of sorption coefficients. Finally, obtaining kinetic information in batch systems can be difficult when sorption is rapid.

### **1.3.2 Column chromatography approach**

As an alternative to batch experiments, packed column techniques are widely used for the study of sorption behaviour (Schwarzenbach et al., 1981, Piatt et al., 1996, Mader et al., 1997, Das et al., 2004). It was developed by James and Phillips (1954) among others, and applied to investigate the sorption to soils and aquifer materials by Schwarzenbach and Westall (1981), Brusseau et al (1989), Mader et al. (1997), Fesch et al. (1998), Bi et al. (2006) and Li et al. (2010). Recently, the practical issues for design, preparation and application of column chromatography approach have been illustrated in detail (Bi et al., 2010). In this approach, a column containing investigated sorbents is firstly packed and then validated (see section 1.3.3). After validation, the chemical of interest in aqueous solution with desired pH and ionic strength under certain temperature is pumped through the column and the concentration of the chemical in the column effluent is monitored over time. If sorption reaches equilibrium and sorption isotherms are (close to) linear, a simple algebraic relationship between  $K_d$  and retardation factor ( $R_f$ ) can be used to back out  $K_d$  values from the obtained breakthrough curves for the investigated concentration range (Piatt et al., 1996, Mader et al., 1997, Bi et al., 2006).

Compared with batch experiments, column studies may more closely simulate the transport of organic compounds in a real soil environment and more readily allow the determination of kinetic information than batch methods. Also, it is a preferable experimental approach, especially for the case that sorption is hardly detectable in the batch experiment (e.g., for the poorly water soluble organic compounds investigated in this study), because it provides a higher sorbent/water ratio than in batch experiment. Furthermore, in the column approach the conditional parameters (such as pH values, ionic strength) affecting sorption are available to be rapidly determined and changed without the problems inherent to batch experiments. Once the column is packed and validated, sorption data can be easily and rapidly generated for many target compounds.

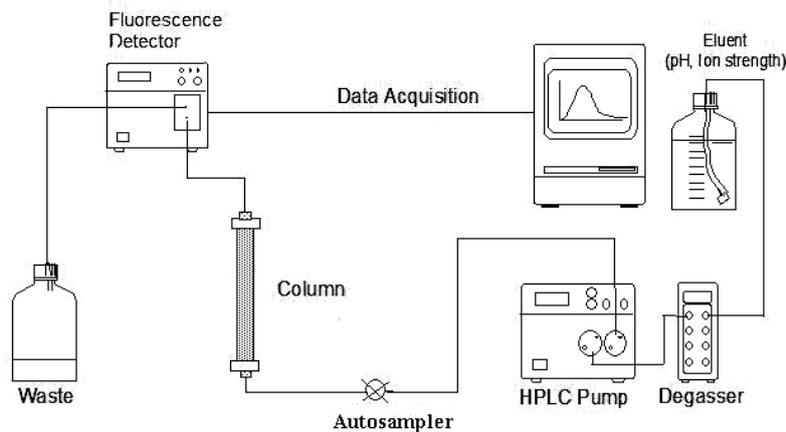


Figure 1-1. Experimental sketch of the column approach (modified from Fesch et al., 1998)

### 1.3.3 Principles of column experiment

#### Column Packing and validation

Some requirements for the column design have been proposed by Relyea (1982). These requirements are: (1) the average flow velocity should be greater than  $1.6 \times 10^{-3}/X_1$  ( $\text{cm} \cdot \text{s}^{-1}$ ), where  $X_1$  is the length of the column; (2) the ratio of the column length to the column diameter should be more than 4; and (3) the ratio of the column diameter to the particle diameter should be no less than 40.

Following the requirements, the column could be packed with the dry packing method. A detailed packing procedure has been issued (Bi et al., 2010).

Validation of the column is done by checking the breakthrough curve of a conservative tracer (reference compound). A symmetric, narrow peak and nearly constant retention time in the breakthrough curve indicates well packed column. Thus, the selection of a suitable conservative tracer is a critical issue in the column experiment since it will influence the final result. An ideal conservative tracer should show no physical-chemical interactions to the stationary phase and be easily detectable. Different tracers were utilized in column experiment, such as thiourea, tritiated water, nitrite, bromide and some fluorescent tracers (Bi et al., 2010). Due to the hydrophilic and UV detectable properties, thiourea is considered as a good tracer and is utilized in current investigations.

After validation, column should be regularly checked by measuring the breakthrough curve of the conservative tracer, especially when the mobile phase and the environmental condition (such as temperature) are changed.

### Local equilibrium and flowrate

According the definition of sorption coefficient ( $K_d$ ) (section 1.1), it describes the distribution of sorbet in/on two phases under equilibrium conditions. Hence it must be independent of the mobile phase flow rate (Bi et al., 2010). In the column approach, to achieve equilibrium is a critical issue. Diffusion through the particle nanopores is the main mechanism in the non-equilibrium sorption process. Generally, the lower the flowrate, the closer the sorption is to equilibrium. A convenient method to judging equilibrium is to carry out the column test at three or more selected flowrates, and to calculate the respecting apparent sorption coefficient ( $K_d'$ ) from each experiment. By plotting  $K_d'$  vs. flowrate, the intercept obtained from regressed  $K_d'$  line is considered as the equilibrium  $K_d$ . Thus if the calculated sorption coefficients  $K_d'$  at a certain selected flowrate is within the error margin of extrapolated intercept, it indicates that equilibrium is achieved at that flowrate.

### Retardation Factor and sorption coefficient $K_d$

The dead time ( $t_o$ ) of column system is determined by the breakthrough curve of a conservative tracer. In the calculation of the retardation factor ( $R_f$ ), the traveling time ( $t'$ ) through the injector and connecting capillary between the injector and detector should be subtracted from the measured retention time ( $t$ ) (Equation 1-3). A general expression for the retardation factor is shown in Equation 1-4 (Zheng and Bennett, 1997). When the Freundlich isotherm is assumed,  $R_f$  can be represented by Equation 1-5. If the sorption isotherm is linear,  $R_f$  and  $K_d$  are proportional to each other (Equation 1-6).

$$R_f = \frac{t - t'}{t_o - t'} \quad (1-3)$$

$$R_f = 1 + \frac{\rho_b}{\theta} \cdot \frac{\partial C_s}{\partial C_w} \quad (1-4)$$

$$R_f = 1 + \frac{\rho_b}{\theta} \cdot K_f \cdot n \cdot C_w^{n-1} \quad (1-5)$$

$$R_f = 1 + \frac{\rho_b}{\theta} \cdot K_d \quad (1-6)$$

Where  $\rho_b$  and  $\theta$  are the bulk density and porosity of the sorbent, respectively.

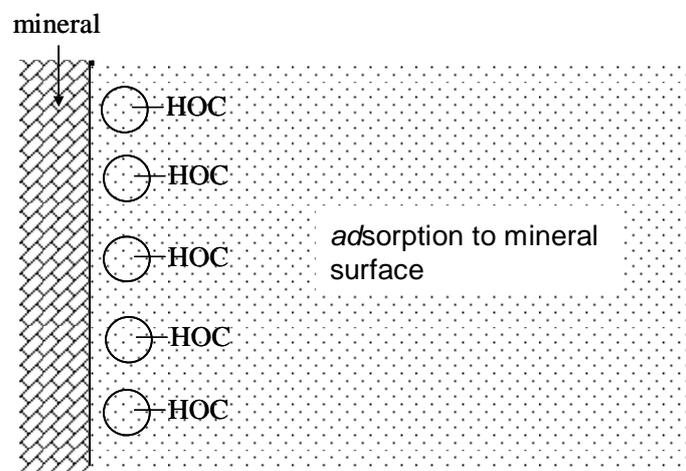
#### 1.4 Sorption mechanisms of HOCs to inorganic surfaces

Partitioning (*absorption*) and *adsorption* are the general terms to describe the sorption processes, which are the two potential mechanisms to explain sorption of HOCs to inorganic surfaces. Typically, the sorption mechanism is considered as adsorption (Fig. 1-2 a). However, adsorption of organic compounds from aqueous solutions to a hydrophilic inorganic surface would require these organic sorbates to displace water molecules already adhering to the polar surface. Since apolar and weakly monopolar organic compounds do not substantially interact via hydrogen bonding, these organic sorbates can not interact with polar surfaces as effectively as water can. Hence, surface adsorption from water to fully water-wet hydrophilic solids probably does not explain the sorption of apolar and weakly monopolar organic compounds to minerals (Schwarzenbach et al., 2003).

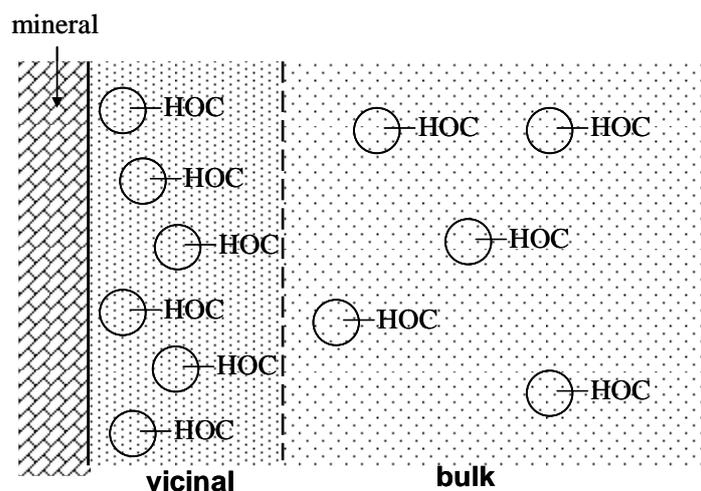
Another possibility is that water molecules near the hydrophilic inorganic surfaces are more organized than corresponding molecules located in the bulk solutions (such surface-ordered water layer are called vicinal water, see Fig. 1-2 b). The organic solutes may interact with the vicinal water layer but not directly with the mineral surface, which is conceptually corresponding to absorption. Note that such a conceptualization still requires the support of more experimental data. However, until now, the sorption mechanism of HOCs to inorganic surfaces has received rather little study. Therefore, identification of the sorption mechanism is an essential task for the better understanding of sorption behaviour to mineral surfaces submerged in water.

It is very important to distinguish the sorption mode for environmental analysis and practical requirements, because the sorption mode determines the predictive method and accurate procedures for estimating the sorption behaviour in sorbent-water system. Recently, the ratio of the sorbent-air / sorbent-water distribution coefficients of n-alkanes to that of cycloalkanes with the same number of carbon atoms ( $K_n/K_c$ ) was proposed to be

indicative of the mode of sorption ( $K_n/K_c < 1$  indicates absorption, while  $\sim 1$  indicates adsorption) (Endo et al., 2008, 2009). Introducing the indicative parameter in this work might help us to better understand the sorption mechanisms of HOCs to inorganic surfaces.



(a)



(b)

Figure 1-2. Schematic illustration of sorption mode: (a) adsorption; (b) absorption (adapted from Schwarzenbach et al., 2003)

### 1.5 Scanning electrochemical microscopy (SECM)

Sorption to laboratory glass walls is important in analysis of HOCs in water since it influences the overall mass balance. Due to sorption, the HOC solution may not be homogenous. More HOC molecules accumulate near the glass surface in or on the vicinal water phase. In this region, the concentration is relatively higher than in the bulk solution,

creating a concentration gradient from the surface towards the bulk. A means for a characterization of this concentration gradient in-situ may provide us with a key to understand the mechanism of sorption of HOCs to inorganic surfaces.

For this purpose, we need to utilize and refine a suitable method for highly spatially resolved analysis of compounds in the sub-micrometer range. A method that recently has attracted much attention for its capabilities of measurements at very high spatial resolution is scanning electrochemical microscopy (SECM). SECM is an electro-chemical imaging technique that allows mapping in-situ the topography of surfaces through the electrodes. Taking advantage of the precisely movable tips of ultramicroelectrodes (UMEs), SECM offers spatially resolved electrochemical measurements and became a sensitive analytical tool for mapping the distribution of chemical species at distinct areas in solution, at interfaces, membranes (Bard et al., 2001) and inside thin polymer films (Schröck et al., 2005).

## **1.6 References**

- Ackerman, A. H., Hurtubise, R. J., 2000, The effects of adsorption of solutes on glassware and Teflon in the calculation of partition coefficients for solid-phase microextraction with 1PS paper. *Talanta* 52, 853-861
- Bard, A. J., Mirkin, M. V., Eds. 2001, Scanning Electrochemical Microscopy. Marcel Dekker: New York,
- Bi, E., Schmidt, T. C., Haderlein, S. B., 2006, Sorption of heterocyclic aromatic compounds to reference soils: column studies for process identification. *Environ. Sci. Technol.* 40, 5962-5970.
- Bi, E., Schmidt, T. C., Haderlein, S. B. 2007. Environmental factors influencing sorption of heterocyclic aromatic compounds to soil. *Environ. Sci. Technol.* 41, 3172-3178
- Bi, E., Schmidt, T. C., Haderlein, S. B., 2010, Practical issues relating to soil column chromatography for sorption parameter determination. *Chemosphere* 80, 787-793
- Brusseau, M.L., Rao, P.S.C., Jessup, R.E. and Davidson, J.M., 1989. Flow interruption: A method for investigating sorption nonequilibrium. *J. Contam. Hydrol.* 4, 223-240.

- Chiou, C. T., 2002. Partition and adsorption of organic contaminants in environmental systems. John Wiley & Sons.
- Chiou, C. T., Peters, L. J., Freed, V. H., 1979, A physical concept of soil-water equilibria for nonionic organic compounds. *Science* 206, 831–832.
- Chiou, C. T., Porter, P. E., Schmedding, D. W. 1983, Partition equilibria of nonionic organic compounds between soil organic matter and water. *Environ. Sci. Technol.* 17, 227-231.
- Das, B.S., Lee, L.S., Rao, P.S.C. and Hultgren, R.P., 2004. Sorption and degradation of steroid hormones in soils during transport: Column studies and model evaluation. *Environ. Sci. Technol.* 38, 1460-1470.
- Delle Site, A., 2001, Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. a review. *J. Phys. Chem. Ref. Data.* 30, 187-439.
- Doucette, W.J., 2003. Quantitative structure-activity relationships for predicting soil-sediment sorption coefficients for organic chemicals. *Environ. Toxicol. Chem.* 22, 1771-1788.
- Endo, S., Grathwohl, P., Schmidt, T.C., 2008, Absorption or Adsorption? Insights from molecular probes n-alkanes and cycloalkanes into modes of sorption by environmental solid matrices. *Environ. Sci. Technol.* 42, 3989-3995
- Endo, S., Grathwohl, P., Haderlein, S. B., Schmidt, T.C., 2009, Characterization of sorbent properties of soil organic matter and carbonaceous geosorbents using n-alkanes and cycloalkanes as molecular probes. *Environ. Sci. Technol.* 43, 193-400
- Fesch, C., Simon, W., Haderlein, S.B., Reichert, P. and Schwarzenbach R.P., 1998, Nonlinear sorption and nonequilibrium solute transport in aggregated porous media: Experiments, process identification and modeling. *J. Contam. Hydrol.* 31, 373-407.
- Grathwohl, P., 1990, Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: Implications on Koc correlations. *Environ. Sci. Technol.* 24, 1687-1693.

- Huang, W., Schlautman, M. A., Weber, W. J., Jr. 1996, A distributed reactivity model for sorption by soils and sediments. 5. the influence of near-surface characteristics in mineral domains. *Environ. Sci. Technol.* 30, 2993-3000.
- Hundal, L. S., Thompson, M. L., Laird, D. A., Carmo, A. M., 2001, Sorption of phenanthrene by reference smectites. *Environ. Sci. Technol.* 35, 3456-3461.
- James, D. H. and Phillips, C. S. G., 1954, The Chromatography of Gases and Vapors, Part III, The Determination of Adsorption Isotherms. *J. Chem. Soc.* 1066-1070.
- Li, B., Qian, Y., Bi, E., Chen, K., Schmidt, T. C., 2010, Sorption behavior of phthalic acid esters on reference soils evaluated by soil column chromatography. *CLEAN – Soil, Air, Water*, 38, 425–429
- Luthy, R. G., Aiken, G. R., Brusseau, M. L. et al., 1997, Sequestration of hydrophobic organic contaminants by geosorbents, *Environ. Sci. Technol.* 31, 3341-3347.
- Mader, B.T., Goss, K.U., Eisenreich, S.J., 1997. Sorption of nonionic, hydrophobic organic chemicals to mineral surfaces. *Environ. Sci. Technol.* 31, 1079-1086.
- Müller, S., Totsche, K. U., Kögel-Knabner, I., 2007, Sorption of polycyclic aromatic hydrocabons to mineral surfaces. *Eur. J. Soil Sci.* 58, 918-931
- Piatt, J. J., Backhus, D. A., Capel, P. D., Eisenreich, S. J., 1996, Temperature-dependent sorption of naphthalene, phenanthrene and pyrene to low organic carbon aquifer sediments. *Environ. Sci. Technol.* 30, 751-760.
- Poerschmann, J., Gorecki, T., Kopinke, F., 2000, Sorption of very hydrophobic organic compounds onto poly (dimethylsiloxane) and dissolved humic organic matter. 1, adsorption or partitioning of VHOC on PDMS-coated solid-phase microextraction fibers—a never-ending story? *Environ. Sci. Technol.* 34, 3824-3830
- Relyea, J. F., 1982, Theoretical and experimental considerations for the use of the column method for determining retardation factors. *Radioactive Waste Management and the Nuclear Fuel Cycle*, 151-166.
- Schröck, K., Schulte, A., Schuhmann, W., 2005, Visualization of the reaction zones between two miscible solutions with potentiometric and amperometric microsensors. *Electroanal.* 17, 489-494.

- Schwarzenbach, R. P., Westall, J., 1981, Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. *Environ. Sci. Technol.* 15, 1360-1367.
- Schwarzenbach, R. P., Gschwend, P. M., Imboden, D.M., 2003. Environmental organic chemistry. 2nd Ed., Wiley: New York.
- Su, Y. H., Zhu, Y. G., Sheng, G., Chiou, C. T., 2006, Linear adsorption of nonionic organic compounds from water on to hydrophilic minerals: silica and alumina. *Environ. Sci. Technol.* 40, 6949-6954
- Tang, C. Y., Fu, Q. S., Gao, D., Criddle, C. S., Leckie, J. O., 2010, Effect of solution chemistry on the adsorption of perfluorooctane sulfonate onto mineral surfaces. *Water Res.* 44, 2654-2662
- ten Hulscher Th. E. M., Cornelissen G. 1996. Effect of temperature on sorption equilibrium and sorption kinetics of organic micropollutants - A review. *Chemosphere*, 32, 609-626.
- Wang, X., Lu, J., Xu, M., Xing, B., 2008, Sorption of pyrene by regular and nanoscaled metal oxide particles: influence of adsorbed organic matter. *Environ. Sci. Technol.* 42, 7267-7272
- Wood, A. L., Bouchard, D. C., Brusseau, M. L., Rao, P. S. C., 1990. Cosolvent effects on sorption and mobility of organic contaminants in soils. *Chemosphere* 20, 575-587.
- Voice, T. C., Rice, C. P., Weber, J. Jr., 1983. Effect of solids concentration on the sorptive partitioning of hydrophobic pollutants in aquatic systems. *Environ. Sci. Technol.* 17, 513-518.
- Xia, G., Pignatello, J., 2001, Detailed Sorption Isotherms of Polar and Apolar Compounds in a High-Organic Soil. *Environ. Sci. Technol.* 35, 84-94
- Yang, Y., Hawthorne, S. B., Miller, D. J., Liu, Y., Lee, M. L. 1998, Adsorption versus absorption of polychlorinated biphenyls onto solid-phase microextraction coatings. *Anal. Chem.* 70, 1866-1869.
- Zheng, C., Bennett, G.D., 1997. Applied Contaminant Transport Modeling: Theory and Practice. Van Nostrand Reinhold, New York.

## **2. Aims**

The general goal of this work is a better understanding of the sorption behavior of non-polar hydrophobic organic compounds (HOCs) to hydrophilic inorganic surfaces in aqueous system. Thus, to identify the sorption mechanisms of HOCs to hydrophilic surfaces and to find a predictive method which enables a-priori decisions how relevant the sorption process could be, are considered as main tasks in this work.

To achieve the goals, four work packages have been carried out by using different methods and instruments. Considering our mainly applicable methods, five polycyclic aromatic hydrocarbons (PAHs, naphthalene, fluorene, phenanthrene, anthracene and pyrene) and four pairs of n- and cycloalkanes (C5 to C8), which are typical HOCs, were chosen as probe compounds and have been investigated.

In the chapter 3 and 4, sorption of selected PAHs to borosilicate glass surface and mineral surfaces (i.e. silica gel, aluminum oxide and titanium oxide) is systematically investigated. The influence of various factors (such as solution chemistry, temperature and surface parameters) to sorption process will be analyzed in detail.

Determination of the sorption mode is an essential issue to understand the sorption mechanism. Therefore, in chapter 5 we focused on characterization of sorption modes in water-mineral systems. Sorption of four pairs of n- and cycloalkanes (C5 to C8) to two mineral surfaces (silica gel and aluminum oxide) were determined. Based on the obtained data, the implications for the sorption mode will be discussed.

Finally, in order to further characterize the near-surface zone on hydrophilic surfaces, a highly spatially resolved technique, scanning electrochemical microscopy (SECM), was applied to determine the concentration gradient from surface to bulk solution and to analyze the sorption process (chapter 6).



### **3. Sorption of polycyclic aromatic hydrocarbons (PAHs) on glass surfaces**

#### **3.1 Introduction**

Polycyclic aromatic hydrocarbons (PAHs) are a group of nonionic hydrophobic organic compounds (HOCs). Because of their widespread environmental prevalence and the high carcinogenic potency (Harvey, 1991; Schwarzenbach et al., 2003), PAHs have received much attention. Numerous research papers have been published on the determination of PAHs in environmental samples, such as air (Lee, 1995; Meijer et al., 2008), sediments and soils (Schneider et al., 2001; Jonker et al., 2007; Pies et al., 2008) and food (Nieva-Cano et al., 2001; McIntosh et al., 2004).

In the environment, PAHs can strongly sorb to solid matrices, such as natural organic matter (NOM) in an aquatic system due to their hydrophobic nature and then accumulate in soils and sediments (Yang et al., 2008). Therefore, sorption of PAHs on soils and sediments has been widely investigated (Carmo et al., 2000; Poerschmann et al., 2000; Xia and Pignatello, 2001). On other hand, sorption of PAHs to organic-free hydrophilic minerals (e.g. silica and alumina) and low-organic-carbon clays was also investigated (Piatt et al., 1996; Mader et al., 1997; Su et al., 2006; Müller et al., 2007) since sorption of PAHs from the aqueous phase to aquifer materials is considered to be important in controlling their concentration and rate of transport in the environment (Schwarzenbach and Westall, 1981; Mader et al., 1997). In those investigations, many researchers reported that mass loss occurred due to strong affinity of PAHs to glass surfaces during equilibration (Carmo et al., 2000; Poerschmann et al., 2000; Ackerman and Hurtubise, 2000). However, in most reports this process was merely held responsible for observed mass losses without experimental corroboration.

In environmental analysis, the sorption of PAHs on untreated glass surfaces is important since the concentrations of these organic compounds are typically very low. Such sorption causes the loss of analytes on glass and might bias subsequent data interpretation. Therefore, characterizing the sorption coefficient of PAHs to glass surfaces is a crucial task for their environmental analysis.

For characterizing the sorption behavior of PAHs, most previous approaches have utilized batch experiments. Although the batch experiment is conceptually simple, it may yield also unreliable sorption data, if analytes show weak sorption or poor solubility, which cause difficulties in precisely detecting the solid-phase concentration or the difference between initial and equilibrium aqueous concentration of the solute (Bi et al., 2006). Furthermore, batch experiment is a time-consuming process. Alternatively, column experiments can be used to determine the sorption of HOCs (Piatt et al., 1996; Mader et al., 1997). Hence, based on our experience with soil column chromatography (Bi et al., 2006, 2010; Li et al. 2010); the HPLC type column method was applied to these investigations. Moreover, based on the column method, various conditions such as solution chemistry (e.g. ionic strengths, cosolvent and solution pH), temperature and coated glass surface were completely studied.

Aims of this study were (i) to develop the column method and compare the results of batch and column experiments (ii) to determine the sorption coefficient ( $K_d$ ) of a series of selected PAHs at the glass-water interface; (iii) to characterize the influence of solution chemistry, temperature and coated surface on sorption; (iv) to evaluate correlations between  $\log K_d$  and the physicochemical parameters, such as subcooled water solubility ( $\log S_w$ ) of selected PAHs.

## **3.2 Materials and methods**

### **3.2.1 Materials**

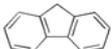
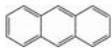
#### **Chemicals**

Five PAHs were selected as probe compounds. Physico-chemical properties of these are listed in table 3-1. Thiourea, naphthalene, methanol,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , sodium hydroxide, fluorene, phenanthrene and pyrene were purchased from Sigma-Aldrich. Anthracene was obtained from Alfa Aesar GmbH. Hydrochloric acid (min. 37%) was purchased from KMF Company. Fluorene, phenanthrene and pyrene were recrystallized in analytical grade ethanol and dried prior to use. The purity of other compounds were above 99% and used without further purification. PAH stock solutions were prepared in methanol at varying concentrations, and all solutions were diluted with Milli-Q grade water (Resistance >18 M $\Omega$ ) and stored in dark under ambient condition.

## Sorbents

Glass beads for the column method were obtained from Bischoff (Part No.: 0010Z000HY300, particle size 30  $\mu\text{m}$ , nonporous, BET-determined specific surface area 1.05  $\text{m}^2/\text{g}$ ). Laboratorial glasswares (100 mL volumetric flasks with glass stoppers, 60 mL glass vials with glass stoppers, borosilicate, BRAND GmbH, Wertheim, Germany) and glass beads obtained from Sigma-Aldrich (Lot. No.: 087K0693, particle size 212-300  $\mu\text{m}$ , BET-determined specific surface area 0.69  $\text{m}^2/\text{g}$ ) were used in batch experiments. Prior to use, all glass beads were washed in methanol and diluted HCl solution in order to remove organic and inorganic impurities, rinsed in Milli-Q water and then dried at 250  $^{\circ}\text{C}$ .

**Table 3-1 Physico-chemical data of probe compounds <sup>a</sup>**

Compound (abbr.)	Structure	Molar Mass (g/mol)	$\log S_w$ ( $\text{mol}/\text{m}^3$ )
Thiourea (THU)		64	3.35 <sup>b</sup>
naphthalene (NAP)		128	-0.09
fluorene (FLU)		166	-1.17
phenanthrene (PHE)		178	-1.57
anthracene (ANT)		178	-1.87
pyrene (PYR)		202	-2.44

a. Data collected from Ma et al., (2010), b. Data from database SRC. <http://www.syrres.com/>

## 3.2.2 Methods

### 3.2.2.1 Column method

Column analysis was done by a standard HPLC system equipped with quaternary pump, diode array detector, fluorescence detector, degasser, auto sampler and column oven (Shimadzu, Duisburg, Germany). The column oven can control temperatures from 5 to 85

°C. A SPD-M10A diode array detector was used for the detection of THU, and the PAHs were measured by RF-10A fluorescence detector, which was installed after the diode array detector in series. The whole setup of the column method followed the sketch proposed by Fesch et al., 1998. Analyses were run at 25 °C, and the injection volume was 5 µL. The concentrations of the injected solutions for THU were in the range of 40-100 mg/L, analyzed aqueous solutions of PAHs were lower than 70% of the saturated subcooled water solubility of each compound. Flow rate was selected based on the consideration of performing the experiments as quickly as possible, though at the same time ensuring equilibrium partitioning behaviour has been achieved. In column experiments, flow rates of 0.05 mL/min, 0.1 mL/min, and 0.2 mL/min were investigated, respectively. Comparing results at various flow rates showed that the retardation factors at 0.05 mL/min and 0.1 mL/min were similar but decreased at 0.2 mL/min. This suggests that at a flow rate lower than 0.1 mL/min, sorption was very close to equilibrium. Regarding time consumption, 0.1 mL/min was chosen in all column experiments. The pH value of the effluent was measured online by 827 pH lab meter (Metrohm, Herisau, Switzerland). THU was chosen as conservative tracer due to its hydrophilic properties and no significant ion exchange (Fesch et al., 1998). The dead time of system ( $t_0$ ) was determined by injection of thiourea solution with 40 mg/L at a flow rate of 0.1 mL/min. Traveling time ( $t'$ ) through the injector and connecting capillary between the injector and diode array detector was  $0.90 \pm 0.01$  min; traveling time from the injector to the additionally connected fluorescence detector was  $1.90 \pm 0.01$  min. Traveling time should be subtracted from measured retention time ( $t$ ), which is achieved by using the half mass method, when calculating the retardation factor ( $R_f$ ):

$$R_f = \frac{t - t'}{t_0 - t'} \quad (3-1)$$

Previous reports (Mader et al., 1997; Su et al., 2006; Müller et al., 2007) showed that sorption isotherms of PAHs on mineral surfaces were linear. Thus,  $K_d$  can be calculated according to the following equation:

$$R_f = 1 + \frac{\rho_b}{\theta} K_d \quad (3-2)$$

where  $\rho_b$  is the bulk density and  $\theta$  is the porosity of the packed column

The glass bead column was packed with the dry packing method. In order to prevent further compression during experiments that could cause peak broadening by extra-column void volume, a high pressure pump was used to compress the column during the packing process. The packed column had a bulk density and porosity of 1.73 g/cm<sup>3</sup> and 0.35, respectively (Stainless steel column 53 mm long, 3 mm internal diameter, Bischoff, Leonberg, Germany).

Temperature effect experiments were carried out by using various column oven temperatures in a range from 15 to 40 °C. According to the van't Hoff equation, the enthalpy change  $\Delta H$  and entropy change  $\Delta S$  for sorption were calculated:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{R T} \quad (3-3)$$

Where  $\Delta S$  is entropy change [kJ/ (mol·K)];  $\Delta H$  is enthalpy change [kJ/mol]; R is gas constant [8.3145 J/ (mol·K)]; T is temperature [K].

#### **3.2.2.2 Batch method**

In order to validate our obtained  $K_d$  values in column method, sorption of anthracene to glass beads and of pyrene to glass beads and laboratorial glasswares were measured in batch experiments. The sorption of other three PAHs to glass surface was very weak and reliable results could not be achieved in batch experiments.

For sorption to glass beads, we chose 50-mL glass vials with glass stoppers as bulk containers. The main procedure was: 4 g of glass beads were mixed with 10 mL aqueous solution of PAHs at various concentrations and containing 0.005 M CaCl<sub>2</sub> to adjust ionic strength. The investigated concentration ranges of anthracene and pyrene were 5-20 µg/L and 20-90 µg/L, respectively. These PAH solutions were produced by spiking with methanol stock solutions, but keeping the concentration of methanol in solution low than 0.1% (v/v) in order to prevent cosolvent interactions. The bulk containers were shaken in a shaking waterbath (GFL 1086, Gesellschaft für Labortechnik mbH, Burgwedel, Germany) at 120 rpm (25 °C) for two days to achieve sorption equilibrium (Su et al., 2006; Müller et al., 2007). After equilibration of the system, the liquid and solid phases were separated by centrifugation and 2 mL of supernatant was extracted in 1 mL n-hexane by shaking for 30 minutes. Solute concentration was quantified by GC-MS (GCMS-QP5050, Shimadzu,

Duisburg, Germany) under the following conditions: HP-5MS capillary column (0.25 mm × 30 m, 0.25 µm thick), Helium 5.0 as carrier gas, flow rate at 0.5 mL/min, injector temperature at 250 °C, interface temperature at 300 °C, SIM mode, and electron ionisation (EI). The temperature program for anthracene and pyrene analyses, respectively, started at 160 °C, held for 2 minutes and increased to 280 °C at a rate of 10 °C per minute. After reaching 280 °C, the temperature was held for 5 minutes. For quality control, reference experiments were carried out at the same time and with the same procedure in vials containing no sorbents. Assuming no mass loss from the containers, e.g., by volatilization, the fraction of adsorbed probe compounds on glass beads and the vial surface can be calculated by using mass balance equations. From quality control experiments, the adsorbed mass on vial surfaces can be calculated and then be subtracted in the sorption coefficient calculation.

For sorption on laboratorial glassware, the same procedure was carried out in 100-mL volumetric flasks and 50-mL glass vials with 20 mL aqueous solutions of PAHs (containing 0.005 M CaCl<sub>2</sub>). By using mass balance equations, again the adsorbed mass can be calculated.

The sorption coefficient is defined as:

$$K_d = C_s \text{ (ng/cm}^2\text{)} / C_w \text{ (ng/mL)} \quad (3-4)$$

where  $C_s$  is equilibrium concentration of compound on glass surface and  $C_w$  is equilibrium concentration of compound in aqueous solution

#### **3.2.3 Mass recovery**

Solute recovery was evaluated by the peak area comparison approach. The peak area obtained from the glass beads column was compared with that from measurement without column using the same equipment. Recovery of thiourea was 97-102%, naphthalene, fluorene and phenanthrene were 92-105%. Recovery of anthracene and pyrene were 89-101% and 83-95%, respectively. All compounds were almost completely recovered in the effluents.

### 3.3 Results and discussion

#### 3.3.1 Sorption coefficient $K_d$

The sorption coefficients ( $K_d$ ) of selected PAHs on glass surfaces with different methods are listed in Table 3-2.

Our batch experiment results showed that sorption of anthracene and pyrene on untreated glass surface was isothermally linear over the investigated concentration ranges, which corroborates previous findings (Mader et al., 1997; Su et al., 2006; Müller et al., 2007).  $K_d$  values of pyrene on laboratorial glassware had a large deviation, because the submerged surface areas were rather small in our experiments, thus the sorbed solute was too small to be quantified relative to the standard error of the measurements.

**Table 3-2 Comparison of sorption coefficients  $K_d$  of PAHs on glass surfaces obtained with column and batch method**

Compound	Column method <sup>a</sup>		Batch method <sup>b</sup>	
	$K_d$ (mL/cm <sup>2</sup> )	$K_d$ (mL/g)	$K_d$ (mL/cm <sup>2</sup> )	R <sup>2</sup>
naphthalene	$5.53 \pm 0.95 \times 10^{-6}$	$0.06 \pm 0.01$	n. d.	
fluorene	$6.40 \pm 0.76 \times 10^{-5}$	$0.67 \pm 0.08$	n. d.	
phenanthrene	$2.03 \pm 0.09 \times 10^{-4}$	$2.13 \pm 0.09$	n. d.	
anthracene	$2.18 \pm 0.12 \times 10^{-4}$	$2.28 \pm 0.13$	$2.15 \pm 0.44 \times 10^{-4}$ <sup>c</sup> (15)	0.973
pyrene	$9.06 \pm 0.44 \times 10^{-4}$	$9.51 \pm 0.46$	$1.32 \pm 0.21 \times 10^{-3}$ <sup>c</sup> (20)	0.992
			$0.77 \pm 0.19 \times 10^{-3}$ <sup>d</sup> (18)	0.981

a. 0.005 M CaCl<sub>2</sub> solution was used as mobile phase.

b. 0.005 M CaCl<sub>2</sub> solution as background solution was used in batch experiments.

c. sorption on glass beads (Sigma-Aldrich).

d. sorption on laboratorial glassware; Number of data points in batch experiments given in parentheses, and error is defined as SD; n.d. not determined. Concentration ranges were 50-800 µg/L for naphthalene and fluorene, 50-500 µg/L for phenanthrene, 5-20 µg/L for anthracene and 20-90 µg/L for pyrene

Comparison of the  $K_d$  values of anthracene and pyrene achieved in batch and column experiments indicated that our column results were in agreement. However, for other investigated PAHs, we could not achieve  $K_d$  values in batch experiments, since sorption was rather weak and the surface area of the glass beads used in batch experiments was limited.

In column experiments, we observed that sorption of PAHs to glass surfaces was significant, except for naphthalene. This indicated that at certain conditions, the mass loss due to sorption on glass surfaces should be corrected in the final calculation. For example, the measured  $K_d$  value of pyrene was  $9.16 \times 10^{-4}$  mL/cm<sup>2</sup>. Assuming tolerance of mass loss is 5%, which requires  $C_w > 95\% C_0$  ( $C_w$  is equilibrium concentration of pyrene and  $C_0$  is initial concentration of pyrene). If the volume of solution is  $V$  mL and the contacted surface area is  $S$  cm<sup>2</sup>, using the following mass balance equation

$$C_s \cdot S + C_w \cdot V = C_0 \cdot V \quad (3-5)$$

in combination with equation (3-4), we conclude that the ratio of  $V/S$  should be greater than 19 times of  $K_d$ , that is in this case 0.017 mL/cm<sup>2</sup>. Otherwise, the sorbed mass of pyrene on vial glass is above 5%, and the mass loss should be taken into account.

Based on the measured  $K_d$  values in Table 3-2, it was found that the correlation of  $K_d$  (mL/cm<sup>2</sup>) of five PAHs to that of the subcooled water solubility  $S_w$  (mol/m<sup>3</sup>) was linear in logarithmic coordinates (Fig. 3-1):

$$\log K_d = 0.94 (-\log S_w) - 5.31 \quad (R^2 = 0.987) \quad (3-6)$$

This corroborates results reported by Müller et al. (2007) who used quartz as sorbent and found a very similar relationship:  $\log K_d = 0.95 (-\log S_w) - 5.82$  ( $R^2 = 0.977$ ). Another similar relationship was also observed in studies of sorption of naphthalene, phenanthrene and pyrene on low organic carbon aquifer sediments, medium-grained sand (Piatt et al., 1996):  $\log K_d = 0.89 (-\log S_w) - 5.67$  ( $R^2 = 0.996$ ). The small variation among values was likely due to different sorbents and different ionic strength in these studies.

This linear correlation may help to predict the sorption of other PAHs to glass surfaces. For example, for benzo[a]pyrene ( $\log S_w = 4.24$ ) according to equation (3-6),  $K_d$  can be calculated as  $4.74 \times 10^{-2}$  mL/cm<sup>2</sup>. Again, assuming 5 % mass loss is tolerated, the  $V/S$  ratio should be greater than 19 times  $K_d$  as demonstrated above, which is 0.90 mL/cm<sup>2</sup>. Some typical  $V/S$  ratios are listed in Table 3-3. We can clearly see that  $V/S$  ratios of

normally used glass vials are less than 0.5. Based on our calculation, if untreated glass containers are used in PAH analysis, mass loss of highly hydrophobic PAHs can not be neglected and should be corrected in the final results.

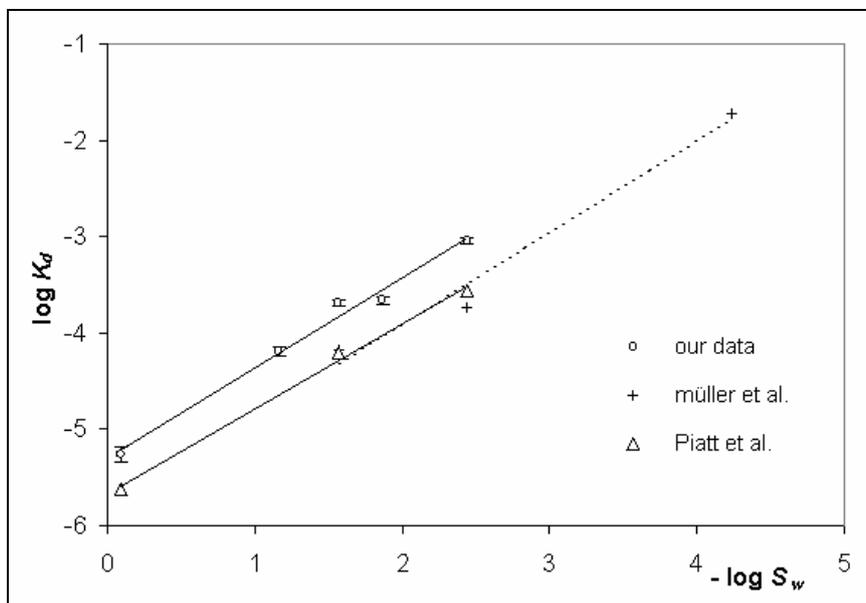


Fig.3-1 Relationship between  $\log K_d$  and  $-\log S_w$ . (our results, 0.005M  $\text{CaCl}_2$  as mobile phase; Müller et al. (2007), compounds: phenanthrene, pyrene and benz[a]pyrene, 0.001M  $\text{KClO}_4$  and  $2 \times 10^{-6}$ M  $\text{AgNO}_3$  as background solution; Piatt et al. (1996), compound: naphthalene, phenanthrene and pyrene, 0.001 M  $\text{NaHCO}_3$  as background solution)

**Table 3-3 Ratios of solution volume to contacted surface area (V/S) of frequently used glassware**

Glassware	Diameter (cm)	Nominal full volume (mL)	V/S ( $\text{mL}/\text{cm}^2$ )	
			full-filled	half-filled
8mm crimp top vial	0.8 <sup>a</sup>	0.8	0.18	0.16
11mm crimp top vial	1.1 <sup>a</sup>	2	0.24	0.21
20mm headspace vial	2.0 <sup>a</sup>	20	0.46	0.43
1L sample storage bottle	10.8 <sup>b</sup>	1000	2.16	1.81

a. data collected from online catalogue of BGB Analytik AG <http://www.bgb-shop.de/home.php>

b. own measurements.

### 3.3.2 Effect of solution chemistry

#### Ionic strength

Ionic strength effects have been investigated using different concentrations of  $\text{CaCl}_2$  (varied from 0.001 M to 0.1 M). Results of these measurements for PHE (at concentration 50 and 200  $\mu\text{g/L}$ , triplicates) and PYR (at concentration of 25 and 50  $\mu\text{g/L}$ , triplicates) are shown in Fig. 3-2. The  $K_d$  values were found to increase significantly with changing  $\text{CaCl}_2$  from 0 to 0.005 M; for example, by running with 0.005 M  $\text{CaCl}_2$  as mobile phase,  $K_d$  increased by 34% and 62% for phenanthrene and pyrene, respectively. This phenomenon could be explained by the “salting-out” effect. Adding ions in solution created a more organized water structure around the cations, which requires more cavity energy for PAHs to dissolve in solution than in regular water. Thus, the activity coefficients of PAHs in water decreased, and consequently an increase of  $K_d$  values occurred.

However, increasing the ionic strength beyond 0.17 (i.e., a 0.005 M calcium chloride solution) did not affect  $K_d$  values any more. This phenomenon has been observed in PHE and PYR at all investigated concentrations, which could not be explained by or only by the “salting-out” effect. Other specific interactions, such as complex formation interactions may also be relevant (Zhu et al., 2004; Keiluweit and Kleber, 2009). However, the detailed mechanism still needs further investigations.

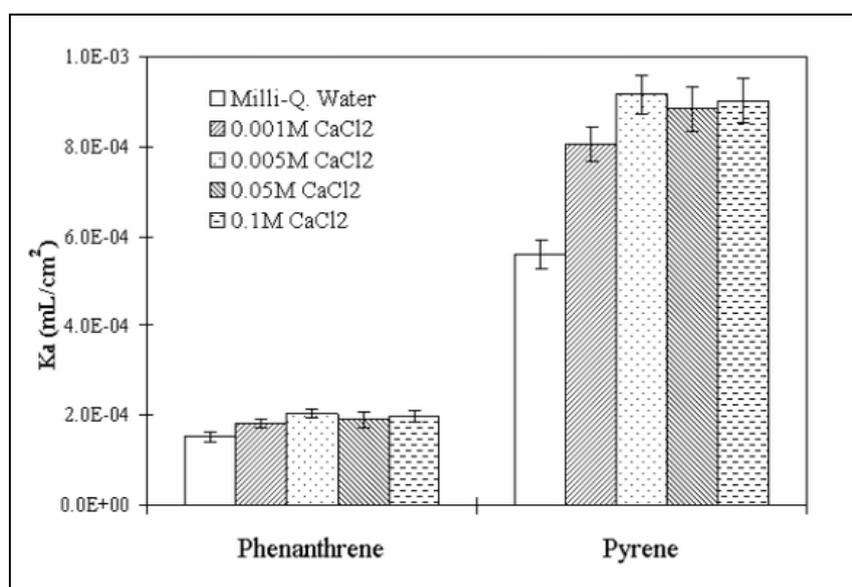


Fig.3-2 Effect of  $\text{Ca}^{2+}$  concentration on the sorption of PHE and PYR to glass (at 25 °C; flowrate 0.1 mL/min; injection volume 5 $\mu\text{L}$ )

### Cosolvent effect

The presence of a water-miscible organic solvent in water may have a significant influence on the  $K_d$  values due to the cosolvent effect (Delle Site, 2001). In previous work, typically the working solutions of hydrophobic organic compounds have been prepared by spiking with its methanol stock solution (Piatt et al., 1996; Müller et al., 2007). In order to quantify to which extent the presence of methanol influences measured  $K_d$  values, methanol-water mixtures with different ratios were used in our investigations. As shown in Table 3-4, the retardation factor increased with the decrease of fraction of methanol in the mobile phase. When the fraction of methanol in water was lower than 0.5% (v/v), both retardation factors of PHE and PYR were very close to those obtained in Milli-Q water, which indicated that no significant cosolvent effect occurred if the concentration of methanol in water was less than 0.5% (v/v). However, our results also show that even in the presence of cosolvent methanol at 10% (v/v), the  $K_d$  values decreased only by around a factor of 2.

**Table 3-4 Determined retardation factors of PAHs at different methanol-water ratios in column method**

Mobile phase (Methanol: Water)	PHE		PYR	
	$R_f$	$K_d$ (mL/g)	$R_f$	$K_d$ (mL/g)
25: 75	$1.27 \pm 0.07$	$0.05 \pm 0.01$	$1.95 \pm 0.06$	$0.19 \pm 0.01$
10: 90	$4.83 \pm 0.10$	$0.77 \pm 0.02$	$14.39 \pm 0.21$	$2.71 \pm 0.04$
5: 95	$5.75 \pm 0.08$	$0.96 \pm 0.02$	$21.76 \pm 0.34$	$4.20 \pm 0.06$
0.5: 99.5	$8.87 \pm 0.19$	$1.59 \pm 0.04$	$30.61 \pm 0.82$	$5.99 \pm 0.16$
Milli-Q water	$8.99 \pm 0.21$	$1.62 \pm 0.04$	$30.42 \pm 0.55$	$5.95 \pm 0.11$

The concentrations of PHE and PYR were 200  $\mu\text{g/L}$  and 50  $\mu\text{g/L}$ , respectively; triplicates; error is defined as SD;  $R_f$ , retardation factor.

Recall the relationship of V/S ratio and  $K_d$  values in 3.3.1, where we have shown that the V/S ratio should be greater than 19 times  $K_d$ . Again taking benzo[a]pyrene as an example and assuming a similar dependency on cosolvent concentration, its  $K_d$  value in 10 % (v/v) methanol will decrease to  $2.37 \times 10^{-2}$  mL/cm<sup>2</sup>, thus the V/S ratio of the glass container should be above 0.44. Comparing this value with the listed V/S ratios in Table 3-3, the mass loss in 8 mm and 11 mm crimp top vial would be above 5 %, which suggests that for highly hydrophobic PAHs such as benzo[a]pyrene, even adding 10 % of methanol in water may not be sufficient to suppress sorption to the glass surface in vials.

#### **Solution pH**

Using various pH values (pH at 3, 5, and 8) in the mobile phase (adjusted by using HCl and NaOH solutions), no significant effect on the  $K_d$  value of phenanthrene was observed and the  $K_d$  value of pyrene only slightly increased towards lower pH (less than a factor of 1.5). Applying the statistical t-test in the measured results at different pH, there was no significant difference. The reason might be that the surface charge of glass in our investigated pH range (from 3 to 8) is still negative, since the points of zero charge of glass were reported less than 2 (Lokar and Ducker, 2004). This corroborates previous findings that sorption of PAHs to mineral surfaces (i.e. silica, alumina) had no marked dependence on solutions' pH (Mader et al., 1997; Su et al., 2006).

#### **3.3.3 Effect of Temperature**

The influence of temperature on the sorption of PAHs on glass surfaces is shown in Fig. 3-3 (concentrations of investigated PAHs were 200 µg/L for NAP, FLU and PHE, 10 µg/L for ANT and 50 µg/L for PYR, respectively). All data were obtained using CaCl<sub>2</sub>-0.005M solution as mobile phase. Sorption coefficients decreased with increasing temperature. Based on Fig. 3-3, according to the van't Hoff equation (equation 3-3), the enthalpy changes ( $\Delta H$ ) for FLU, ANT, PHE and PYR sorption on glass surfaces were -5.5, -5.7, -6.5, and -4.1 kJ/mol respectively. Generally, the  $\Delta H$  of van der Waal's forces is between -4 and -8 kJ/mol (Delle Site, 2001). The values of  $\Delta H$  suggest that the sorption of PAHs on glass surfaces was dominated by nonspecific interactions (i.e., van der Waal's forces).

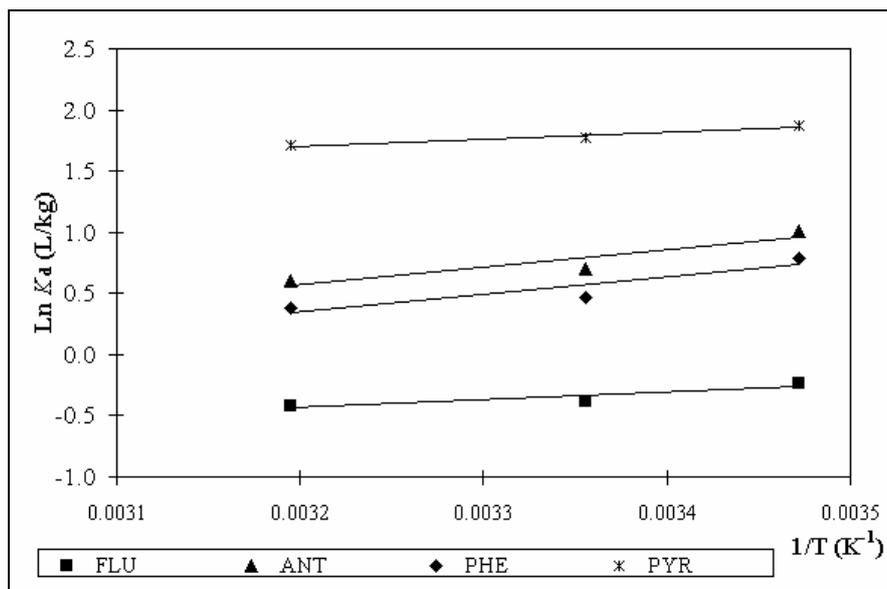


Fig. 3-3 Effect of temperature on the sorption of PAHs to glass (at 15, 25, 40°C; mobile phase: 0.005M CaCl<sub>2</sub>; flowrate 0.1 mL/min; injection volume 5μL)

### 3.3.4 Effect of surface property

The use of silane coated (silanized) glassware is usually considered to be able to significantly reduce the mass loss of hydrophobic organic compound, since sorption to the coated surface was found weaker than to uncoated glassware (Langenfeld et al., 1996; Yang et al., 1998). Our results by using chlorotrimethylsilane coated glass beads instead of uncoated glass beads in the column method corroborated these findings. When using silanized glass, retardation factors decreased by 46% and 21% for PHE and PYR (PHE at 200 μg/L and PYR at 50 μg/L) respectively. Again, recalling the relationship of V/S ratio and K<sub>d</sub> value and taking benzo[a]pyrene as an example, a 21% decrease of K<sub>d</sub> leads to a required V/S ratio above 0.8, which is much higher than the V/S ratio of commonly used glassware listed in Table 3-3. These results indicate that for highly hydrophobic PAHs, mass loss to silanized glass surfaces may still be relevant.

Furthermore, based on molecular interactions between surface and compounds in aqueous solution the reason for the decrease of K<sub>d</sub> on silanized glass is hard to explain. The detailed mechanism needs further investigations.

### **3.4 Implications**

To minimize the impact of mass loss caused by sorption on glass surfaces is a critical issue in analysis since the sorption of PAHs to glass was found difficult to eliminate. In this paper, we summarized that the mass loss of PAHs was closely related to the sorption coefficient  $K_d$  and the ratio of solution volume to contacted surface area ( $V/S$ ). If a mass loss of  $w$  % is tolerated, the  $V/S$  ratio needs to be larger than  $(100/w - 1) \times K_d$ . Utilizing equation (3-6) this can be modified to:  $V/S > (100/w - 1) \times (0.94 (-\log S_w) - 5.31)$  for water with cosolvent content  $< 0.5\%$  in unsilanized glass vials. Although less comprehensive data are available as a first approximation the required  $V/S$  is reduced by a factor of 1.2 using silanized glass and by a factor of 1.5 and 2 by using 5 and 10% methanol as cosolvent.

### **3.5 Acknowledgements**

Financial support for this work was provided by the Deutsche Forschungsgemeinschaft (DFG, grant SCHM2350/2-1). Thanks to Mrs. Claudia Schenk for the BET surface area determination. Thanks also to Erping Bi and Satoshi Endo for helpful discussions throughout this work.

### **3.6 References**

- Ackerman, A. H., Hurtubise, R. J., 2000, The effects of adsorption of solutes on glassware and Teflon in the calculation of partition coefficients for solid-phase microextraction with 1PS paper. *Talanta* 52, 853-861
- Bi, E., Schmidt, T. C., Haderlein, S. B., 2006, Sorption of heterocyclic aromatic compounds to reference soils: column studies for process identification. *Environ. Sci. Technol.* 40, 5962-5970.
- Bi, E., Schmidt, T. C., Haderlein, S. B., 2010, Practical issues relating to soil column chromatography for sorption parameter determination. *Chemosphere*, 80, 787-793

- Carmo, A. M., Hundal, M. L., Thompson, M. L., 2000, Sorption of hydrophobic organic compounds by soil materials: application of unit equivalent freundlich coefficients. *Environ. Sci. Technol.* 34, 4363-4369
- Delle Site, A., 2001, Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. a review. *J. Phys. Chem. Ref. Data.* 30, 187-439.
- Fesch, C., Simon, W., Haderlein, S. B., Reichert P., Schwarzenbach R.P., 1998, Nonlinear sorption and nonequilibrium solute transport in aggregated porous media: Experiments, process identification and modeling. *J. Contam. Hydrol.* 31, 373-407.
- Harvey, R. G., 1991, Polycyclic Aromatic Hydrocarbons: Chemistry and Carcinogenicity, Cambridge Monographs on Cancer Research, Cambridge University Press, 1st edition.
- Jonker, M. T. O., Van der Heijden, S. A., Kreitinger, J. P., Hawthorne, S. B., 2007, Predicting PAH bioaccumulation and toxicity in earthworms exposed to manufactured gas plant soils with solid-phase microextraction. *Environ. Sci. Technol.* 41, 7472-7478
- Keiluweit, M., Kleber, M., 2009, Molecular-level interactions in soils and sediments: the role of aromatic  $\pi$ -systems. *Environ. Sci. Technol.* 43, 3421-3429.
- Langenfeld, J. J., Hawthorne, S. B., Miller, D. J., 1996, Quantitative Analysis of Fuel-Related Hydrocarbons in Surface Water and Wastewater Samples by Solid-Phase Microextraction. *Anal. Chem.* 68, 144-155.
- Lee, H. K., 1995, Recent applications of gas and high-performance liquid chromatographic techniques to the analysis of polycyclic aromatic hydrocarbons in airborne particulates. *J. Chromatogr. A*, 710, 79-92

- Li, B., Qian, Y., Bi, E., Chen, H., Schmidt, T. C., 2010, Sorption behavior of phthalic acid esters on reference soils evaluated by soil column chromatography. *CLEAN-Soil Air Water*, 38, 425–429
- Lokar, W. J. and Ducker, W. A., 2004, Proximal adsorption at glass surfaces: ionic strength, pH, chain length effects. *Langmuir*, 20, 378-388
- Ma, Y.-G., Lei, Y. D., Xiao, H., Wania, F., Wang, W.-H., 2010, Critical review and recommended values for physical-chemical property data of 15 polycyclic aromatic hydrocarbons at 25 °C. *J. Chem. Eng. Data* 55, 819-825
- Mader, B. T., Goss, K.-U., Eisenreich, S. J., 1997, Sorption of nonionic, hydrophobic organic chemicals to mineral surfaces. *Environ. Sci. Technol.* 31, 1079-1086
- McIntosh, A. D., Moffat, C. F., Packer, G., Webster L., 2004, Polycyclic aromatic hydrocarbon (PAH) concentration and composition determined in farmed blue mussels (*Mytilus edulis*) in a sea loch pre- and post-closure of an aluminum smelter. *J. Environ. Monitor.* 6, 209-218
- Meijer, S. N., Sweetman, A. J., Halsall, C. J., Jones, K. C., 2008, Temporal trends of polycyclic aromatic hydrocarbons in the U.K. atmosphere: 1991-2005. *Environ. Sci. Technol.* 42, 3213-3218
- Müller, S., Totsche, K. U., Kögel-Knabner, I., 2007, Sorption of polycyclic aromatic hydrocarbons to mineral surfaces. *Eur. J. Soil Sci.* 58, 918-931
- Nieva-Cano, M. J., Rubio-Barroso, S., Santos-Delgado, M. J., 2001, Determination of PAH in food samples by HPLC with fluorimetric detection following sonication extraction without sample clean-up. *Analyst*, 126, 1326-1331
- Piatt, J. J., Backhus, D. A., Capel, P. D. and Eisenreich, S. J., 1996, Temperature-dependent sorption of naphthalene, phenanthrene and pyrene to low organic carbon aquifer sediments. *Environ. Sci. Technol.* 30, 751-760.

- Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T. A., Hofmann, T., 2008, Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soil. *Chemosphere*, 72, 1594-1601
- Poerschmann, J., Gorecki, T., Kopinke, F., 2000, Sorption of very hydrophobic organic compounds onto poly (dimethylsiloxane) and dissolved humic organic matter. 1, adsorption or partitioning of VHOC on PDMS-coated solid-phase microextraction fibers—a never-ending story? *Environ. Sci. Technol.* 34, 3824-3830
- Schneider, A. R., Stapleton, H. M., Cornwell, J., Baker, J. E., 2001, Recent declines in PAH, PCB, and toxaphene levels in the northern great lakes as determined from high resolution sediment cores. *Environ. Sci. Technol.* 35, 3809-3815
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2003. Environmental Organic Chemistry. 2<sup>nd</sup> Ed., Wiley: New York.
- Schwarzenbach, R. P., Westall, J., 1981, Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. *Environ. Sci. Technol.* 15, 1360-1367.
- Su, Y. H., Zhu, Y. G., Sheng, G., Chiou, C. T., 2006, Linear adsorption of nonionic organic compounds from water on to hydrophilic minerals: silica and alumina. *Environ. Sci. Technol.* 40, 6949-6954
- Xia, G. and Pignatello, J., 2001, Detailed sorption isotherms of polar and apolar compounds in a high-organic soil. *Environ. Sci. Technol.* 35, 84-94
- Yang, Y., Hawthorne, S. B., Miller, D. J., Liu, Y., Lee, M. L., 1998, Adsorption versus absorption of polychlorinated biphenyls onto solid-phase microextraction coatings. *Anal. Chem.* 70, 1866-1869.

Yang, Y., Ligouis, B., Pies, C., Achten, C., Hofmann, T., 2008, Identification of carbonaceous geosorbents for PAHs by organic petrography in river floodplain soils.

*Chemosphere*, 71, 2158-2167

Zhu, D. Q., Herbert, B. E., Schlautman, M. A., Carraway, E. R., Hur, J., 2004a, Cation-pi bonding: A new perspective on the sorption of polycyclic aromatic hydrocarbons to mineral surfaces.

*J. Environ. Qual.* 33, 1322–1330.

## 4. Sorption of polycyclic aromatic hydrocarbons (PAHs) on mineral surfaces in aqueous solution: an HPLC type column study.

### 4.1 Introduction

Sorption is the primary chemical-physical process controlling the transport and fate of nonionic hydrophobic organic compounds (HOCs) in environmental solids. As a group of typical nonionic HOCs, polycyclic aromatic hydrocarbons (PAHs) are of concern because many are suspected mutagens, teratogens and carcinogens (Harvey, 1991; Piatt et al., 1996; Schwarzenbach et al., 2003). Thus, knowledge about their behavior and fate in environmental matrices is of high importance for environmental risk assessment. Consequently, many investigations about the sorption of PAHs have been carried out and published in the past years (Schwarzenbach et al., 1981; Chiou et al., 1983; Kile et al., 1995; Carmo et al., 2000; Hundal et al., 2001, Schneider et al., 2001; Yang et al., 2008).

In the environment, sorption of PAHs is dominated by organic matter. However, for solids containing no or small amounts of organic matter (as a rule-of-thumb less than 0.1% (w/w)), sorption to mineral surfaces becomes the major process. Therefore, sorption to organic-free hydrophilic minerals (e.g. silica and alumina) and low-organic-carbon clays was also actively investigated (Huang et al., 1996; Piatt et al., 1996; Mader et al., 1997; Su et al., 2006; Müller et al., 2007; Wang et al., 2008).

Batch methods are typically used in sorption investigations. However, this is very time consuming since sorption processes are often observed to require periods of weeks or even months to reach equilibrium (Huang et al., 1996; Delle Site A., 2001). With regard to sorption on mineral surfaces, if sorption is weak or the surface area is limited, a relatively low mass of solutes is sorbed on the solids, which may cause difficulties in accurate quantification. As an alternative, column chromatography can be used to quickly determine the sorption coefficient ( $K_d$ ) of organic compounds and closely simulate the change of  $K_d$  under different natural condition. Although column chromatography has been applied in the investigation of sorption of nonionic hydrophobic organic compounds to low organic carbon aquifers or mineral surfaces (Piatt et al., 1996; Mader et al., 1997), the results always showed that  $K_d$  values obtained in column chromatography (columns with 2.22 - 2.54 cm diameter) were 3-10 times lower than those achieved in batch

experiments (Piatt et al., 1996). Based on our experiences with soil column chromatography (Bi et al., 2010; Li et al. 2010) and comparable results in our previous studies (Qian et al., 2010), the HPLC type column method was applied in these investigations.

In some previous reports (Huang et al., 1996; Wang et al., 2008), sorption of HOCs to minerals in aqueous solution was considered as an absorption in the vicinal water layer, a more ordered water layer in the direct vicinity of hydrophilic surfaces that extends up to approximately 100 nm (Drost-Hanson, 1978), but not directly an adsorption on mineral surfaces. Recently, however, a more extended ordered water layer at hydrophilic surfaces has been proposed (Zheng et al., 2006). The volume of vicinal water is proportionally related to the surface area of the minerals. Consequently, the amount of absorbed solutes in this “special water” should be also proportionally affected by surface area. Therefore, the influence of mineral surface area, especially for porous materials, should significantly impact sorption and needs to be analyzed.

The aims of this study were: (i) to determine the sorption coefficient ( $K_d$ ) of five PAHs to three minerals by using HPLC type column method; (ii) to compare the column method obtained  $K_d$  values to that measured from previous batch methods; (iii) to analyze the influence of surface area of sorbents and various environmental factors, such as temperature, solution pH, and ionic strength, on  $K_d$  values.

## **4.2 Materials and methods**

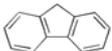
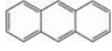
### **4.2.1 Materials**

#### **Chemicals**

Five PAHs were selected as probe compounds and their physicochemical properties are listed in table 4-1. Thiourea, naphthalene, methanol,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , sodium hydroxide, fluorene, phenanthrene and pyrene were purchased from Sigma-Aldrich. Anthracene was obtained from Alfa Aesar GmbH. Hydrochloric acid (min. 37%) was purchased from KMF Company. Fluorene, phenanthrene and pyrene were recrystallized in analytical grade ethanol and dried prior to use. The purity of all other compounds was above 99 % and they were used without further purification. PAH stock solutions were prepared in

methanol at varying concentrations, and all solutions were diluted with Milli-Q grade water and stored under ambient condition.

**Table 4-1 Physico-chemical data of probe compounds <sup>a</sup>**

Compound (abbr.)	Structure	Molar Mass (g/mol)	log $S_w$ (mol/m <sup>3</sup> )
Thiourea (THU)		64	3.35 <sup>b</sup>
naphthalene (NAP)		128	-0.09
fluorine (FLU)		166	-1.17
phenanthrene (PHE)		178	-1.57
anthracene (ANT)		178	-1.87
pyrene (PYR)		202	-2.44

a. Data collected from Ma et al., (2010),

b. Data from database SRC. <http://www.syrres.com/>,  $S_w$  subcooled water solubility at 25 °C

### Sorbents

Three different minerals were used in the whole study. Silica gel, with a particle size of 63-100  $\mu\text{m}$  and an average pore size of 6 nm, was obtained from Merck (Darmstadt, Germany). The BET-N<sub>2</sub> determined surface area of this sample was 435 m<sup>2</sup>/g. The aluminum oxide was purchased from Bischoff (Leonberg, Germany), which has a particle size of 10  $\mu\text{m}$  and a BET surface area of 116 m<sup>2</sup>/g. Titanium dioxide was obtained from Sachtleben (Duisburg, Germany), which has a particle size of 10  $\mu\text{m}$  and average pore size of 6 nm. The BET determined surface area was 96.7 m<sup>2</sup>/g. Prior to use, all sorbents were washed in methanol to remove organic impurities, rinsed in Milli-Q water and then dried at 250 °C.

In order to investigate the influence of surface area to  $K_d$  value, two additional minerals were investigated. Silica gel 10-120, with a particle size of 10  $\mu\text{m}$  and an average pore

size of 12 nm, was purchased from Bischoff (Loenberg, Germany). The BET-N<sub>2</sub> determined surface area of this sample was 300 m<sup>2</sup>/g. And titanium dioxide 10-300 was obtained from Sachtleben (Duisburg, Germany), which has a particle size of 10µm and average pore size of 30 nm. The BET determined surface area was 19.7 m<sup>2</sup>/g.

#### **4.2.2 Method**

Experiments were carried out in a standard HPLC system equipped with quaternary pump, diode array detector, fluorescence detector, degasser, auto sampler, column oven (all Shimadzu, Duisburg, Germany). The column oven can control temperatures from 5 to 85°C. A SPD-M10A diode array detector was used for the detection of THU, and the PAHs were measured by RF-10A fluorescence detector, which was installed after the diode array detector in series. Measurements were run at 25°C (except for the study of temperature effect), and the injection volume was 10 µL. Every experiment was carried out in triplicate. The concentrations of the injected solutions for THU were in the range of 40-100 mg/L, concentrations of aqueous solutions of PAHs were lower than 66% of the maximum water solubility of each compound. The flow rate was selected to approach sorption equilibrium in the column as far as possible. In column experiments, flow rates of 0.05, 0.1, 0.15, and 0.2 mL/min were investigated, respectively. Comparing results at various flow rates showed that the retardation factors at a flow rate of 0.1 mL/min or lower were similar but decreased at 0.15 mL/min and 0.2 mL/min. This suggests that at a flow rate lower than 0.1 mL/min, sorption equilibrium is approached. Regarding time consumption, 0.1 mL/min was chosen in all column experiments. The pH value of the effluent was measured online by 827 pH lab meter (Metrohm, Herisau, Switzerland). Thiourea was chosen as conservative tracer due to its hydrophilic properties and no significant ion exchange (Fesch et al., 1998). The dead time ( $t_0$ ) of the system was determined by injection of thiourea solution with 40 mg/L at a flow rate of 0.1 mL/min. Traveling time ( $t'$ ) through the injector and connecting capillary between the injector and diode array detector was  $0.90 \pm 0.01$  min; traveling time from the injector to the additionally connected fluorescence detector was  $1.90 \pm 0.01$  min. Traveling time is subtracted from measured retention time ( $t$ ) according to equation 1. Retention time  $t$  is derived from breakthrough curves by using the half mass method for subsequent calculation of the retardation factor ( $R_f$ ) as discussed previously (Bi et al., 2010).

$$R_f = \frac{t-t'}{t_o-t'} \quad (4-1)$$

Previous reports (Mader et al., 1997; Su et al., 2006; Müller et al., 2007, Wang et al., 2008) showed that sorption isotherms of PAHs on mineral surfaces were linear. Thus,  $K_d$  can be calculated according to the following equation:

$$R_f = 1 + \frac{\rho_b}{\theta} * K_d \quad (4-2)$$

where  $\rho_b$  is the bulk density and  $\theta$  is the porosity of the packed column.

The column was packed with the dry packing method. In order to prevent further compression during experiments that could cause peak broadening, a high pressure pump was used to compress the column during the packing process. The finished packed columns had a bulk density and porosity of 0.53 g/cm<sup>3</sup> and 0.757 for silica gel column, 1.00 g/cm<sup>3</sup> and 0.715 for aluminum oxide column, and 1.22 g/cm<sup>3</sup> and 0.688 for titanium dioxide column, respectively (Stainless steel column 53 mm long, 3 mm inner diameter, Bischoff, Leonberg, Germany).

#### 4.2.3 Mass recovery

Solute recovery was evaluated by the peak area comparison approach: The peak area obtained from the varied column was compared with that from measurement without column using the same equipment. Recovery of THU was 99-100% (n=6), NAP, FLU and PHE were 97-102 % (n=6). Recovery of ANT and PYR were 96-99% and 94-99% (n=9), respectively. All compounds were almost completely recovered in the effluents, indicating no irreversible sorption or mass loss in the system.

### 4.3 Results and discussions

#### 4.3.1 Sorption coefficient $K_d$

The retardation factors of selected PAHs in different columns showed no dependence on the concentration of injected samples (concentration range: 50-1000 µg/L for naphthalene and fluorene, 50-500 µg/L for phenanthrene, 5-20 µg/L for anthracene and 20-90 µg/L for pyrene), which corroborated previous findings of linear sorption isotherms (Huang et al.,

1996; Mader et al., 1997; Su et al., 2006; Müller et al., 2007; Wang et al., 2008). The sorption coefficients ( $K_d$ ) on different minerals calculated with equation (4-2) are listed in Table 4-2.

**Table 4-2 Sorption coefficients  $K_d$  of PAHs on different minerals<sup>a</sup>**

Compound	Silica gel	Aluminum oxide	Titanium dioxide
	$K_d$ (L/kg)	$K_d$ (L/kg)	$K_d$ (L/kg)
naphthalene	$0.67 \pm 0.02$	$0.12 \pm 0.01$	$0.07 \pm 0.02$
fluorene	$3.44 \pm 0.15$	$1.71 \pm 0.12$	$0.59 \pm 0.11$
phenanthrene	$8.22 \pm 0.43$	$3.82 \pm 0.15$	$2.37 \pm 0.12$
anthracene	$11.4 \pm 0.36$	$5.86 \pm 0.14$	$3.43 \pm 0.18$
pyrene	$35.1 \pm 1.64$	$18.4 \pm 0.68$	$10.3 \pm 0.76$

a. 0.005 M CaCl<sub>2</sub> solution was used as mobile phase; at 25°C; flowrate 0.1 mL/min; injection volume 10 µL; error is defined as 1 SD

Comparing our measured  $K_d$  values of phenanthrene and pyrene on silica gel and alumina to literature reported data (batch method) using materials with a similar surface area, the difference was less than a factor of 2 except for pyrene on silica gel. Sorption of higher molecular weight PAHs to glass and Teflon has been reported to be significant (Ackerman et al., 2000; Qian et al., 2010). Therefore, the different experimental procedures utilized in batch method and column method may cause such variations. Another potential reason might be that the investigated silica gels had different surface characteristics (i.e., pore size, surface roughness) despite a similar surface area (Table 4-3).

**Table 4-3 Sorption isotherms of phenanthrene and pyrene to mineral surfaces**

Sorbents	Reference	Surface area (m <sup>2</sup> /g)	Phenanthrene		Pyrene	
			$K_d$ (L/kg)	$K_{d SA}$ (L/m <sup>2</sup> ) <sup>a</sup>	$K_d$ (L/kg)	$K_{d SA}$ (L/m <sup>2</sup> ) <sup>a</sup>
<b>Silica gel</b>						
Silica gel 40	Huang et al., 1996	521	5.9	1.14x10 <sup>-5</sup>	n.d.	
Silica gel	Su et al., 2006	563	6.48	1.15x10 <sup>-5</sup>	18.9	3.35x10 <sup>-5</sup>
Silica gel	our data	434	8.22	1.89x10 <sup>-5</sup>	35.1	8.09x10 <sup>-5</sup>
<b>Alumina</b>						
Alumina	Su et al., 2006	155	2.28	1.53x10 <sup>-5</sup>	12.0	7.42x10 <sup>-5</sup>
Alumina	our data	116	3.82	3.29x10 <sup>-5</sup>	18.4	1.59x10 <sup>-4</sup>

<sup>a</sup>  $K_{d SA}$ , surface normalized sorption coefficient; Background electrolyte: Huang et al. (1996), 0.01M NaNO<sub>3</sub>; Su et al. (2006), 0.01M CaCl<sub>2</sub>; our data, 0.005M CaCl<sub>2</sub>; n.d. not determined

Based on the measured  $K_d$  values in Table 4-2, it was observed that the correlation of  $K_d$  (L/kg) value of five PAHs to that of the subcooled water solubility  $S_w$  (mol/m<sup>3</sup>) on all investigated minerals was linear in logarithmic coordinates (Fig. 4-1):

Silica gel:  $\log K_d$  (L/kg) = 0.73 (-log  $S_w$ ) - 0.26 ( $R^2 = 0.946$ )

Aluminum oxide:  $\log K_d$  (L/kg) = 0.93 (-log  $S_w$ ) - 0.93 ( $R^2 = 0.991$ )

Titanium dioxide:  $\log K_d$  (L/kg) = 0.94 (-log  $S_w$ ) - 1.23 ( $R^2 = 0.963$ )

Such linear relationships could also be observed from the reported results, for example, for sorption of naphthalene, phenanthrene and pyrene on low organic carbon aquifer sediments in column method (Piatt et al., 1996):  $\log K_d = 0.89 (-\log S_w) - 1.64$  ( $R^2 = 0.996$ ); for sorption of naphthalene, fluoranthene, anthracene and pyrene on aluminum oxide (Mader et al., 1997):  $\log K_d = 0.61 (-\log S_w) - 2.13$  ( $R^2 = 0.976$ ); and for sorption of phenanthrene, pyrene and benz[a]pyrene on quartz (Müller et al., 2007):  $\log K_d = 0.95 (-\log S_w) - 2.34$  ( $R^2 = 0.977$ ). The variation among values might be due to different surface characteristics of sorbents (such as surface area and pore size) in these studies, which are

discussed in more detail in 3.2. Such linear correlations may help to predict the sorption of other PAHs to mineral surfaces.

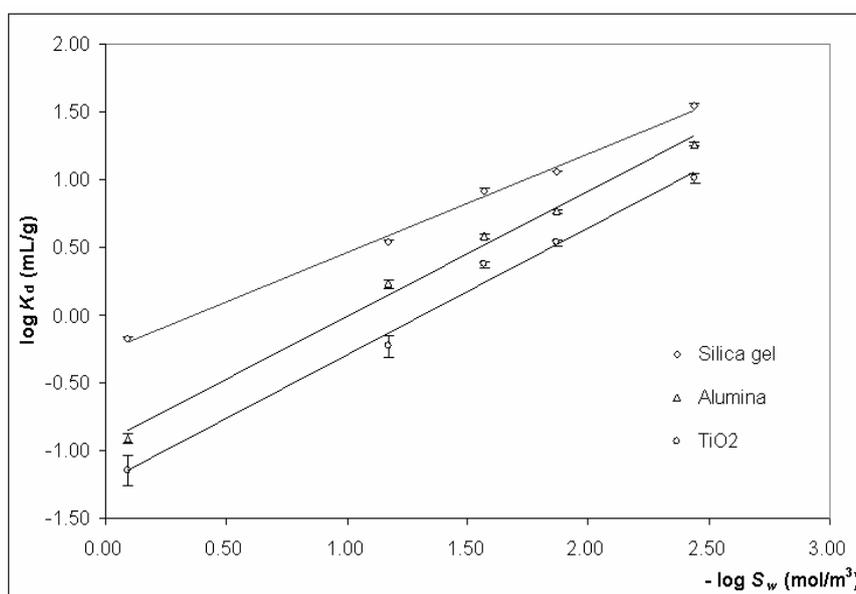


Fig.4-1 Relationship between  $\log K_d$  and  $-\log S_w$  of investigated PAHs on different minerals

#### 4.3.2 Effect of surface characteristics

The surface normalized sorption coefficients in different water-mineral phases are listed in Table 4-4. Generally, surface area normalized sorption coefficients were found that obtained from materials with small surface area were higher than those measured on corresponding materials with high surface area (except data of Huang (1996) on silica and Mader (1997) on alumina).

One possible reason to explain the surface area effect is that the BET-N<sub>2</sub> determined surface area under dry conditions is not equivalent to that in aqueous conditions. Huang et al. (1996) pointed out that most mineral surfaces are neither flat nor perfectly smooth at a molecular scale. The microscopic surface roughness can significantly influence the sorption of N<sub>2</sub> gas molecules in BET measurement but may have little effect on the sorption of larger solute molecules from aqueous phase, since the roughness could be moderated or “smoothed” by sorbed water molecules. Therefore, a part of the BET measured surface area, especially for the sorbents with higher surface area determined in

BET-N<sub>2</sub>, may not be effective for sorption of organic solutes, which leads to a lower surface area normalized  $K_d$  value (Table 4-4). It needs to develop a new definition or method for determination of aqueous effective surface area is critical for further research on sorption, in particular to mineral surfaces.

**Table 4-4 Sorption isotherms of phenanthrene and pyrene to minerals**

Sorbents	particle size (μm)	pore size (nm)	S. A. (m <sup>2</sup> /g)	Phenanthrene $K_{dSA}$ (L/m <sup>2</sup> )	Pyrene $K_{dSA}$ (L/m <sup>2</sup> )	Ref.
Quartz	1		6.53	2.01x10 <sup>-4</sup>		a
	63-2000		0.30	6.57x10 <sup>-4</sup>	1.85x10 <sup>-3</sup>	d
Glass beads	30		1.05	2.03x10 <sup>-3</sup>	9.16x10 <sup>-3</sup>	f
amorphous SiO <sub>2</sub>	1		8.23	5.62 x10 <sup>-5</sup>		a
Silica	63-300	12	314	0.87x10 <sup>-5</sup>		a
	63-300	10	314	1.09x10 <sup>-5</sup>		a
	63-300	4	521	1.14x10 <sup>-5</sup>		a
	100-200	6	563	1.15x10 <sup>-5</sup>	3.35x10 <sup>-5</sup>	c
	10	12	300	2.42x10 <sup>-5</sup>	1.06x10 <sup>-4</sup>	g
	63-100	6	434	1.89x10 <sup>-5</sup>	8.09x10 <sup>-5</sup>	g
Alumina *	1		13.3	2.58x10 <sup>-4</sup>		a
	1		11.14		1.96x10 <sup>-5</sup>	b
	100		155	1.53x10 <sup>-5</sup>	7.42x10 <sup>-5</sup>	c
	0.43		10.9		1.01x10 <sup>-3</sup>	e
	10		116	3.29x10 <sup>-5</sup>	1.59x10 <sup>-4</sup>	g
Titanium dioxide	0.28		7.3		6.85x10 <sup>-4</sup>	e
	10	6	96.7	2.45x10 <sup>-5</sup>	1.07x10 <sup>-4</sup>	g
	10	30	19.7	1.12x10 <sup>-4</sup>	5.63x10 <sup>-4</sup>	g

a. Huang et al., (1996); b. Mader et al., (1997); c. Su et al., (2006); d. Müller et al., (2007); e. Wang et al., (2008); f. Qian et al., (2010); g. our data

S. A., surface area;  $K_{dSA}$ , surface area normalized sorption coefficient; \*, pore size of all alumina was not given by reference or material supplier.

### 4.3.3 Effect of solution chemistry

Solution chemistry, such as ionic strength and solution pH, may play a role in sorption of HOCs on mineral surfaces (Zhu et al., 2004, Tang et al., 2010).

### Ionic strength effect

Ionic strength effects have been investigated using different concentrations of  $\text{CaCl}_2$ . Results of these measurements for PHE (at concentration 50 and 200  $\mu\text{g/L}$ ) and PYR (at concentration 25 and 50  $\mu\text{g/L}$ ) are shown in Fig. 4-2. Ionic strength showed only little effect on the  $K_d$  values on silica and alumina. By running with 0.05 M  $\text{CaCl}_2$  solution instead of Milli-Q grade water as mobile phase, the increase of  $K_d$  values for phenanthrene and pyrene was less than a factor of 1.5. Further increasing the ionic strength did not affect  $K_d$  values. On titanium dioxide, an ionic strength effect was not observed. Generally, our results showed that ionic strength had no significant effect on the sorption of PAHs on investigated mineral surfaces. This conclusion agrees with previous reports that sorption of PAHs to mineral surfaces (i.e. silica, alumina) had no marked dependence on ionic strength (Mader et al., 1997; Su et al., 2006).

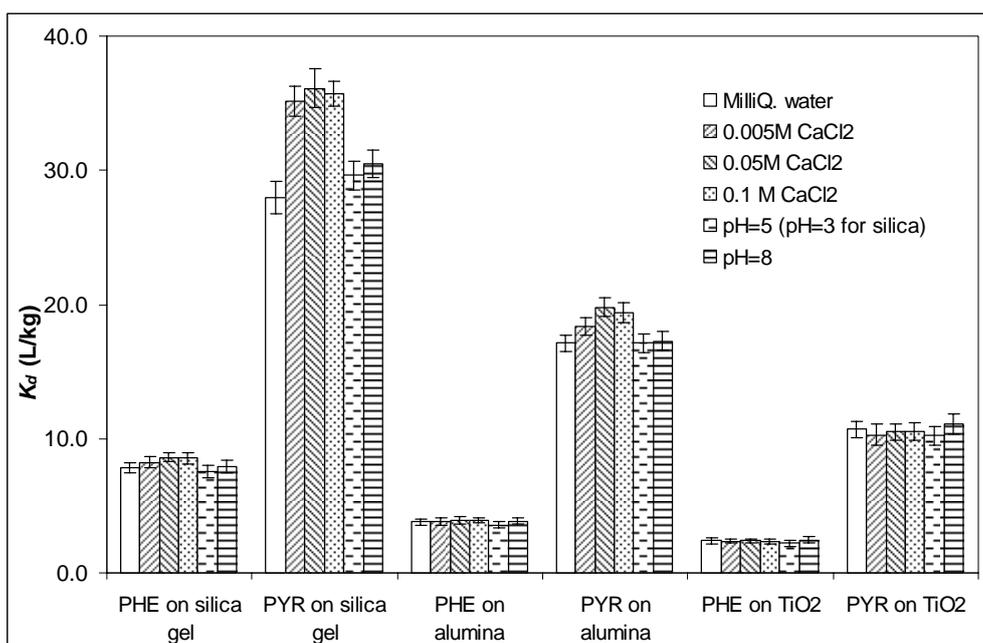


Fig. 4-2 Effect of various mobile phases on the sorption of phenanthrene and pyrene to investigated minerals (at 25°C; flowrate 0.1 mL/min; injection volume 10  $\mu\text{L}$ )

### Solution pH effect

Using various pH values (pH at 3 and 8 for silica gel; 5 and 8 for aluminum oxide and titanium dioxide) in the mobile phase (adjusted by using HCl and NaOH solutions), the  $K_d$

values of PHE and PYR on three mineral surfaces were measured and are shown in Fig. 4-2. Applying the statistical t-test in the measured results at different pH, the difference was not significant. Therefore, we conclude that in our investigated pH ranges, no effect occurred on the  $K_d$  values of all minerals. The reason might be that the change of surface charge in our investigated pH range was not significant, since the PZC of silica and alumina were reported less than 3 and above 8 respectively (Kosmulski, 2004). However, the reported PZC of titanium dioxide was between 6 and 7 (Kosmulski, 2004), in our investigated pH range also no significant change of  $K_d$  values was observed. This corroborates previous findings that sorption of PAHs to mineral surfaces (i.e. silica, alumina) had no marked dependence on solutions' pH (Mader et al., 1997; Su et al., 2006).

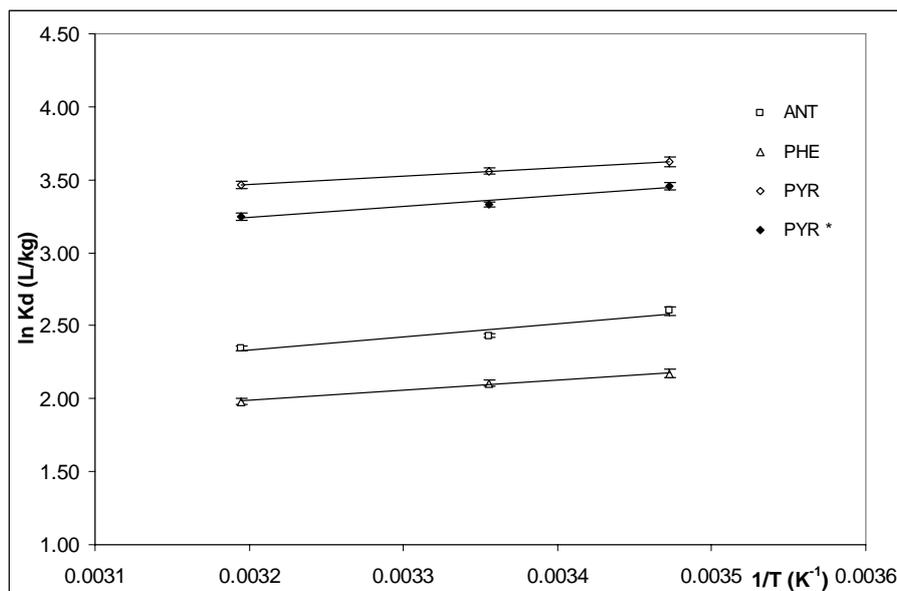
#### 4.3.4 Effect of Temperature

Temperature effect experiments were carried out by using various column oven temperatures in a range from 15 to 40 °C (Concentrations of investigated PAHs were 200 µg/L for PHE, 10 µg/L for ANT and 50 µg/L for PYR, respectively). Based on the van't Hoff equation, the enthalpy change  $\Delta H$  and entropy change  $\Delta S$  for sorption were calculated:

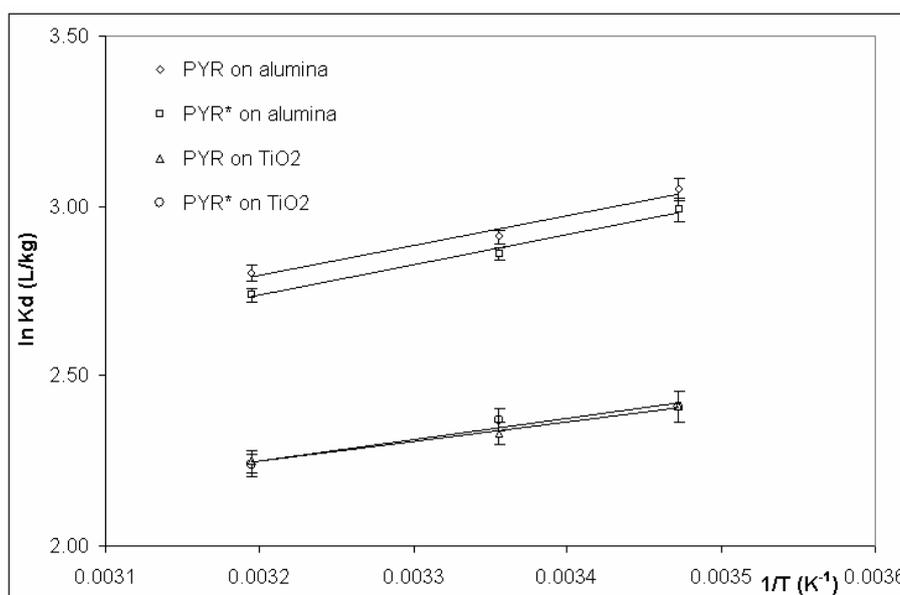
$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{R} * \frac{1}{T} \quad (4-3)$$

Where  $\Delta S$  is entropy change [kJ/ (mol·K)];  $\Delta H$  is enthalpy change [kJ/mol]; R is gas constant [8.3145 J/ (mol·K)]; T is temperature [K].

#### 4. Sorption of PAHs on mineral surfaces



(a)



(b)

Fig. 4-3 Effect of temperature on the sorption of PAHs on different mineral surfaces (a. on silica gel; b. on alumina and  $\text{TiO}_2$ ) at 15, 25, 40°C,  $\text{CaCl}_2$  0.005 M in mobile phase (except for \* marked data: Milli-Q grade water as mobile phase); flowrate 0.1 mL/min; injection volume 10  $\mu\text{L}$ .

The influence of temperature on the sorption of PAHs on three investigated mineral surfaces is shown in Fig. 3. The sorption coefficients decreased with increasing temperature on all investigated minerals. According to equation 3, the enthalpy changes ( $\Delta H$ ) for sorption of ANT, PHE and PYR on silica in 0.005 M  $\text{CaCl}_2$  solution were -7.5, -

5.8, and -4.8 kJ/mol, respectively. The  $\Delta H$  of PYR on alumina and titanium dioxide in 0.005 M  $\text{CaCl}_2$  solution were -7.3 kJ/mol and -5.2 kJ/mol, respectively. Similar enthalpy changes have been found using  $\text{CaCl}_2$  containing mobile phase and Milli-Q grade water. Generally, the  $\Delta H$  of van der Waal's forces is between -4 and -8 kJ/mol (Delle Site, 2001). The values of  $\Delta H$  suggest that the sorption of PAHs on mineral surfaces is dominated by nonspecific interactions (i.e., van der Waal's forces) and fully reversible.

#### **4.4 Conclusions**

A linear relationship between sorption coefficients  $K_d$  and the subcooled water solubility  $S_w$  of investigated PAHs in logarithmic coordinates on all investigated minerals was observed. This relationship may help to predict  $K_d$  values of other PAHs.

On porous material, the most critical factor is surface area, which shows a strongly effect to the sorption coefficients  $K_d$  of investigated PAHs (i. e. particle size and pore size). The  $K_d$  values obtained from various surface area did not show proportion to the surface area, which indicates the effective surface area in aqueous conditions is not equivalent to BET- $\text{N}_2$  determined surface area under dry conditions. Other environmental factors such as ionic strength, solution pH and temperature didn't influence significantly the sorption coefficient  $K_d$ .

#### **4.5 Acknowledgements**

This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG, grant SCHM2350/2-1). Thanks to Claudia Schenk for the BET surface area determination. Special thanks go to Satoshi Endo and Kai-Uwe Goss for their valuable discussions and knowledgeable suggestions.

#### **4.6 References**

Ackerman, A. H., Hurtubise, R. J., 2000, The effects of adsorption of solutes on glassware and Teflon in the calculation of partition coefficients for solid-phase microextraction with 1PS paper. *Talanta* 52, 853-861

- Bi, E., Schmidt, T. C., Haderlein, S. B., 2010, Practical issues relating to soil column chromatography for sorption parameter determination. *Chemosphere* 80, 787-793
- Carmo, A. M., Hundal, M. L., Thompson, M. L., 2000, Sorption of Hydrophobic Organic Compounds by Soil Materials: Application of Unit Equivalent Freundlich Coefficients. *Environ. Sci. Technol.* 34, 4363-4369
- Chiou, C. T., Porter, P. E., Schmedding, D. W., 1983, Partition equilibria of nonionic organic compounds between soil organic matter and water. *Environ. Sci. Technol.* 17, 227-231.
- Delle Site, A., 2001, Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. a review. *J. Phys. Chem. Ref. Data.* 30, 187-439.
- Drost-Hanson, W., 1978, Water at biological interfaces-structural and functional aspects. *Phys. Chem. Liq.* 7, 243-348.
- Fesch, C., Simon, W., Haderlein, S.B., Reichert, P. and Schwarzenbach R.P., 1998, Nonlinear sorption and nonequilibrium solute transport in aggregated porous media: Experiments, process identification and modeling. *J. Contam. Hydrol.* 31, 373-407.
- Harvey, R. G., 1991, Polycyclic aromatic hydrocarbons: Chemistry and carcinogenicity, Cambridge Monographs on Cancer Research, Cambridge University Press, 1st edition,
- Huang, W., Schlautman, M. A., Weber, W. J., Jr. 1996, A distributed reactivity model for sorption by soils and sediments. 5. the influence of near-surface characteristics in mineral domains. *Environ. Sci. Technol.* 30, 2993-3000.
- Hundal, L. S., Thompson, M. L., Laird, D. A., Carmo, A. M., 2001, Sorption of phenanthrene by reference smectites. *Environ. Sci. Technol.* 35, 3456-3461.
- Kile, D. E., Chiou, C. T., Zhou, H., Li, H., Xu, O., 1995, Partition of nonpolar organic pollutants from water to soil and sediment organic matters. *Environ. Sci. Technol.* 29, 1401-1406.
- Kosmulski, M., 2004, pH-dependent surface charging and point of zero charge II. Update. *J. Colloid Interface Sci.* 275, 214-224

- Li, B., Qian, Y., Bi, E., Chen, K., Schmidt, T. C., Sorption behavior of phthalic acid esters on reference soils evaluated by soil column chromatography, *CLEAN – Soil, Air, Water* 2010, 38, 425–429
- Ma, Y.-G., Lei, Y. D., Xiao, H., Wania, F., Wang, W.-H., 2010, Critical review and recommended values for physical-chemical property data of 15 polycyclic aromatic hydrocarbons at 25 °C. *J. Chem. Eng. Data* 55, 819-825
- Mader, B. T., Goss, K.-U., Eisenreich, S. J., 1997, Sorption of nonionic, hydrophobic organic chemicals to mineral surfaces. *Environ. Sci. Technol.* 31, 1079-1086
- Müller, S., Totsche, K. U., Kögel-Knabner, I., 2007, Sorption of polycyclic aromatic hydrocarbons to mineral surfaces. *Eur. J. Soil Sci.* 58, 918-931
- Piatt, J. J., Backhus, D. A., Capel, P. D., Eisenreich, S. J., 1996, Temperature-dependent sorption of naphthalene, phenanthrene and pyrene to low organic carbon aquifer sediments. *Environ. Sci. Technol.* 30, 751-760.
- Qian, Y., Posch, T., Schmidt, T. C., 2010, Sorption of polycyclic aromatic hydrocarbons (PAHs) on glass surfaces. *Chemosphere*. submitted.
- Schneider, A. R., Stapleton, H. M., Cornwell, J., Baker, J. E., 2001, Recent declines in PAH, PCB, and toxaphene levels in the northern great lakes as determined from high resolution sediment cores. *Environ. Sci. Technol.* 35, 3809-3815
- Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M., 2003. Environmental organic chemistry. 2<sup>nd</sup> Ed., Wiley: New York.
- Schwarzenbach, R. P. and Westall, J., 1981, Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. *Environ. Sci. Technol.* 15, 1360-1367.
- Su, Y. H., Zhu, Y. G., Sheng, G., Chiou, C. T., 2006, Linear adsorption of nonionic organic compounds from water on to hydrophilic minerals: silica and alumina. *Environ. Sci. Technol.* 40, 6949-6954
- Tang, C. Y., Fu, Q. S., Gao, D., Criddle, C. S., Leckie, J. O., 2010, Effect of solution chemistry on the adsorption of perfluorooctane sulfonate onto mineral surfaces. *Water Res.* 44, 2654-2662

- Wang, X., Lu, J., Xu, M., Xing, B., 2008, Sorption of pyrene by regular and nanoscaled metal oxide particles: influence of adsorbed organic matter. *Environ. Sci. Technol.* 42, 7267-7272
- Xia, G., Pignatello, J., 2001, Detailed Sorption Isotherms of Polar and Apolar Compounds in a High-Organic Soil. *Environ. Sci. Technol.* 35, 84-94
- Yang, Y., Ligouis, B., Pies, C., Achten, C., Hofmann, T., 2008, Identification of carbonaceous geosorbents for PAHs by organic petrography in river floodplain soils. *Chemosphere*, 71, 2158-2167
- Zheng, J., Chin, W.-C., Khijniak, E., Khijniak, E., Jr., Pollack, G. H., 2006, Surface and interfacial water: Evidence that hydrophilic surfaces have long-range impact. *Adv. Colloid Interface Sci.* 127, 19-27
- Zhu, D. Q., Herbert, B. E., Schlautman, M. A., Carraway, E. R., Hur, J., 2004a, Cation-pi bonding: A new perspective on the sorption of polycyclic aromatic hydrocarbons to mineral surfaces. *J. Environ. Qual.* 33, 1322–1330.

## **5. Characterizing the sorption mode to mineral surfaces in aqueous solution by using alkane and cycloalkane probe compounds**

### **5.1 Introduction**

Sorption of organic compounds to various solid phases has been of great interest in environmental science over the past decades, because sorption controls the concentration and rate of transport in the environment, and may also control the reactions that transform organic compounds (Chiou et al., 1979, Delle Site, 2001, Schwarzenbach et al., 2003). Generally, sorption of organic compounds is dominated by the organic substances in the case of solids containing more than 0.1- 0.2% of organic matter (OM) (Schwarzenbach et al., 1981, Chiou et al., 1983, Su et al., 2006). However, for solids containing virtually no or very low fractions of OM, sorption to mineral surfaces may become significant, even if the overall uptake is weak (Su et al., 2006). Therefore, sorption to organic-free hydrophilic minerals (e.g. silica and alumina) and low-organic-carbon clays was also actively investigated (Piatt et al., 1996, Huang et al., 1996, Mader et al., 1997, Su et al., 2006, Müller et al., 2007). However, the sorption mechanisms are not completely understood.

Two potential mechanisms, *absorption* and *adsorption*, are currently proposed to explain the sorption of nonionic hydrophobic organic compounds (HOCs) to mineral surfaces. In the adsorption model, the nonionic solutes are considered to replace the water molecules which adhere strongly in the layer (monolayer) just out of the mineral surfaces (Schwarzenbach et al., 2003). However, this proposed mechanism may be energetically unfavourable, as the nonionic HOCs can not interact with polar surfaces as effectively as water can. Another suggestion is that a layer of “structurally oriented” water, termed vicinal water (Mader et al., 1997), stretches out of the mineral surface and nonionic solutes may interact with the vicinal water layer but not directly with the mineral surface, which is conceptually corresponding to absorption. Usually, the mode of sorption in water-mineral system is not easy to distinguish, since often a combination of both is observed. However, it is critical to distinguish ab- or adsorption as this information determines how concentrations should be expressed and which sorption models should be used for estimating sorption coefficients of the organic contaminants.

## 5. Characterizing the sorption mode by using alkane and cycloalkane

Roth et al. (2005a, 2005b) proposed poly-parameter linear free energy relationship to elucidate the dominant sorption mode and Goss et al. (2006) used highly fluorinated compounds distinguish ab- and adsorption. Recently, Endo et al. (2008) demonstrated the use of pairs of n-alkanes and cycloalkanes of the same carbon number as molecular probes for the determination of sorption modes from air to sorbents. The mode of sorption of a sorbate from air to a sorbent is determined via the ratio of the sorption coefficient of the n-alkane and the cycloalkane according to:

$$K_n/K_c = (K_{\text{sorbent/air}} \text{ of n-alkane}) / (K_{\text{sorbent/air}} \text{ of cycloalkane}) \quad (5-1)$$

where  $K_{\text{sorbent/air}}$  is the sorbent-air distribution coefficient. A  $K_n/K_c$  ratio  $< 1$  indicates absorption, since according to the cavity model (Goss and Schwarzenbach, 2001); a smaller cavity is required to accommodate the cycloalkanes (Endo et al., 2008). Thus, more cycloalkanes can be held in the cavities than n-alkanes, which causes that the  $K_c$  is greater than  $K_n$ . A  $K_n/K_c$  ratio  $\sim 1$  indicates adsorption (without steric effects) because of the similar dispersion interaction properties of the two compounds. For sorbent-water systems, since the  $K_d$  value is determined by molecular interactions in/on the sorbent phase but also in the water phase, it was pointed out that direct comparison of  $K_d$  values of the n- and cycloalkane was inappropriate (Borisover and Graber, 1997, Goss, 2004, Endo et al., 2009), therefore Eq. 5-1 has to be expanded to:

$$\frac{K_n}{K_c} = \left( \frac{K_d}{K_{aw}} \text{ of n-alkane} \right) / \left( \frac{K_d}{K_{aw}} \text{ of cycloalkane} \right) \quad (5-2)$$

where  $K_d$  is the sorbent-water distribution coefficient and  $K_{aw}$  is the air-water partitioning coefficient of the n-alkane or cycloalkane. As discussed by Endo et al.,  $K_n/K_c$  ratio  $< 1$  is valid for absorption to wet sorbents, too. In contrast,  $K_n/K_c$  ratio  $\geq 1$  could potentially be invalid for adsorption to solid surfaces that are submerged in water, because the sorption to surfaces in aqueous systems may require a cavity in the vicinal water layer on or near the surface of the sorbent and the energy of desorption of water molecules could affect the overall process. In a later study, Endo et al. (2009) showed that  $K_n/K_c$  for sorption to carbonaceous sorbents (e.g., graphite) in water is consistently  $\geq 1$ . However, whether the sorption ratio  $K_n/K_c$  is useful to foster understanding of sorption modes for hydrophilic sorbents (like minerals) fully submerged in water has not been examined yet. Furthermore, sorption of alkanes and cycloalkanes to mineral surfaces has received less attention and

few studies on that exist; therefore, there is a lack of literature data with regard to sorption coefficients.

In order to fill the above-mentioned knowledge gaps, the goals of our study are: (i) to determine sorption isotherms for n- and cycloalkanes in exemplary water-mineral systems (e.g. water-silica and water-alumina); (ii) to evaluate the sorption behavior on both mineral surfaces; and (iii) to establish  $K_n/K_c$  ratios to distinguish sorption modes on both mineral surfaces.

## **5.2 Materials and Methods**

### **5.2.1 Materials**

Four pairs of n- and cyclo-alkanes (C5 to C8) were selected as probe compounds. Physico-chemical properties of these compounds are listed in Table 5-1. Pentane, cyclopentane, hexane, cyclohexane, heptane, cycloheptane, octane, cyclooctane, methanol, calcium chloride and sodium azide were purchased from Sigma-Aldrich. The purity of all these compounds was above 99% and they were used without further purification. Two minerals, silica and aluminum oxide, were used as sorbents in this investigation. Silica gel, with a particle size of 63-100  $\mu\text{m}$  and an average pore size of 6 nm, was obtained from Merck (Darmstadt, Germany). The BET- $\text{N}_2$  determined surface area of this sample was 435  $\text{m}^2/\text{g}$ . The aluminum oxide, short as “alumina”, was purchased from Sigma-Aldrich, which has a particle size of about 100  $\mu\text{m}$  and a surface area of 155  $\text{m}^2/\text{g}$  (manufacturer data). Prior to use, all sorbents were washed in methanol solution in order to remove organic impurities, rinsed with Milli-Q grade water and then dried at 250  $^\circ\text{C}$ . Due to the poor aqueous solubility of the probe compounds, aqueous solutions of these compounds were prepared by dilution of their methanol stock solutions, keeping the residual methanol concentration below 0.1 % in order to prevent co-solvent effects. All solutions were diluted with Milli-Q grade water (Resistance  $>18\text{M}\Omega$ ).

**Table 5-1 Physico-chemical properties of probe compounds at 25 °C**

Compounds	Molar Weight (g/mol)	Water solubility <sup>a</sup> log $S_w$ (mg/L)	log( $K_{aw}$ ) <sup>c</sup>	log( $K_{ow}$ ) <sup>c</sup>
n-Pentane	72.2	1.62	1.69	3.39
n-Hexane	86.2	1.05	1.74	4.00
n-Heptane	100.2	0.55 <sup>b</sup>	1.93	4.66
n-Octane	114.2	-0.13	2.07	5.15
Cyclopentane	70.1	2.19	0.88	3.00
Cyclohexane	84.2	1.74	0.89	3.44
Cycloheptane	98.2	1.48 <sup>b</sup>	0.59 <sup>b</sup>	4.00 <sup>b</sup>
Cyclooctane	112.2	0.90	0.51 <sup>a</sup>	4.45 <sup>a</sup>

a. data collected from supporting information of Endo et al., 2009, freely available via <http://pubs.acs.org>

b. data from database SRC. <http://www.syrres.com/>.

c. data collected from Schwarzenbach et al., 2003.

$K_{aw}$ , Air-water partitioning coefficient;  $K_{ow}$ , Octanol-water partitioning coefficient.

### 5.2.2 Method

Sorption isotherms of selected compounds to mineral surfaces were measured in batch experiments. The 20-mL headspace vials were used as bulk containers. In order to minimize mass loss, aluminum coated crimp caps were utilized. The main procedure was: In a 20-mL headspace vial, 2.5 g of sorbent material (silica or aluminum oxide) was firstly filled. Then, freshly prepared alkane or cycloalkane aqueous solution (directly diluted from corresponding their methanol stock solution) at varied concentrations (maximal up to 50 % of the water solubility) containing 5 mM  $\text{CaCl}_2$  to adjust ionic strength and 100 mg/L  $\text{NaN}_3$  to inhibit microbial activity was introduced into the headspace vial until completely full and the vial was sealed immediately to avoid mass loss by volatilization. For quality control, a reference experiment was carried out simultaneously with the same procedure but without added sorbents. All vials were stored in a water bath at 25°C to

achieve equilibrium. Our previous equilibrium tests showed that there was no statistically significant difference in sorption extent after 3 days, 7 days and 10 days. Thus, 3 days seemed to be sufficient to achieve sorption equilibrium. After equilibration, 5 mL of supernatant was transferred by a 5-mL glass syringe (Poulten & Graf GmbH, Wertheim, Germany) into another empty headspace vial, crimp sealed immediately and stored in a water bath at 25°C. After air-water equilibrium was established, 250µl (pentane/ cyclopentane, hexane/ cyclohexane, heptane/ cycloheptane) or 500µl (octane/ cyclooctane) of the headspace was extracted using a 500µL Pressure Lok® VICI precision syringe (VICI AG, Schenk, Switzerland) and injected into the GC-FID (Shimadzu, GC-FID 2014, Duisburg, Germany) with a Permabond SE-54 capillary (0,25mm inner diameter, 0.5 µm film thickness, 30m length) for analysis. All experiments were carried out in triplicates.

Mass loss caused by volatilization during the solution transfer procedure and sorption on vial surface was assumed to be the same in vials containing sorbents and in reference vials. The sorbent-independent mass loss due to volatilization and sorption on vial glass surfaces can be calculated by using the difference between initially prepared concentration and measured aqueous concentration in the reference experiment. This difference is then subtracted from the aqueous phase concentration in the experiments with sorbents and the corrected concentration is used in the sorption coefficient calculation.

The sorption coefficient is defined as:

$$K_d = C_s \text{ (mg/Kg)} / C_w \text{ (mg/L)} \quad (5-3)$$

where  $C_s$  is equilibrium compound concentration on the solid phase and  $C_w$  is equilibrium compound concentration in aqueous solution.

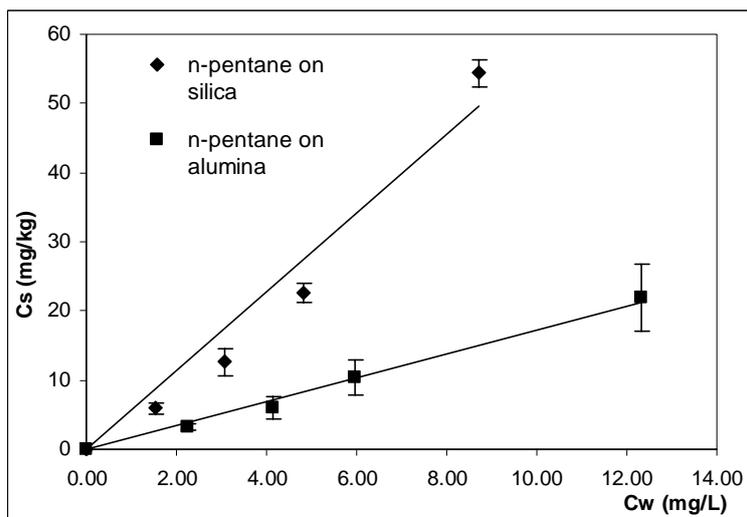
## **5.3 Results and Discussions**

### **5.3.1 Sorption isotherms**

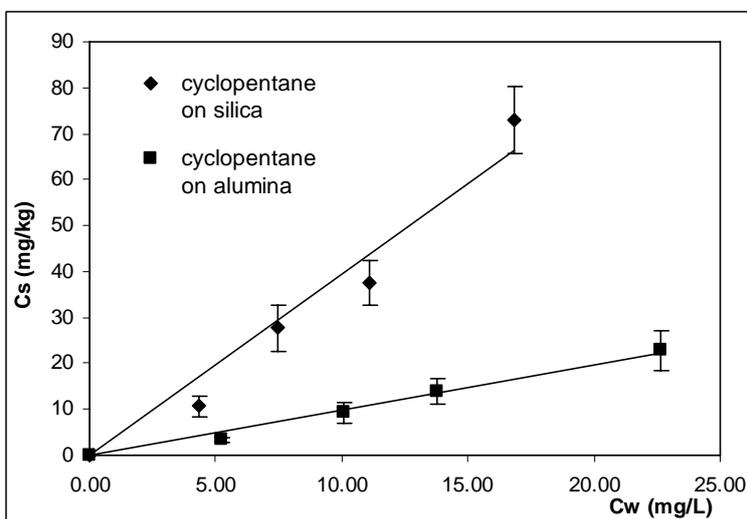
The sorption isotherms of selected n- and cycloalkanes on silica and alumina at 25 °C are presented in Fig. 5-1. Several literatures reported that sorption of HOCs to mineral surfaces was found linear isotherms (Mader et al., 1997, Su et al., 2006, Müller et al., 2007). Our results corroborate this assumption. The larger deviations in the measured data

## 5. Characterizing the sorption mode by using alkane and cycloalkane

(Fig. 5-1) might be caused by the evaporation loss in the transfer procedure in experiment, since the investigated compounds are very volatile. The obtained corresponding sorption coefficients are listed in Table 5-2. As shown in Table 5-2, the surface normalized  $K_d$  values on silica gel and aluminium oxide were found no significant difference, which indicated that there is no difference in surface affinity between these two sorbents.

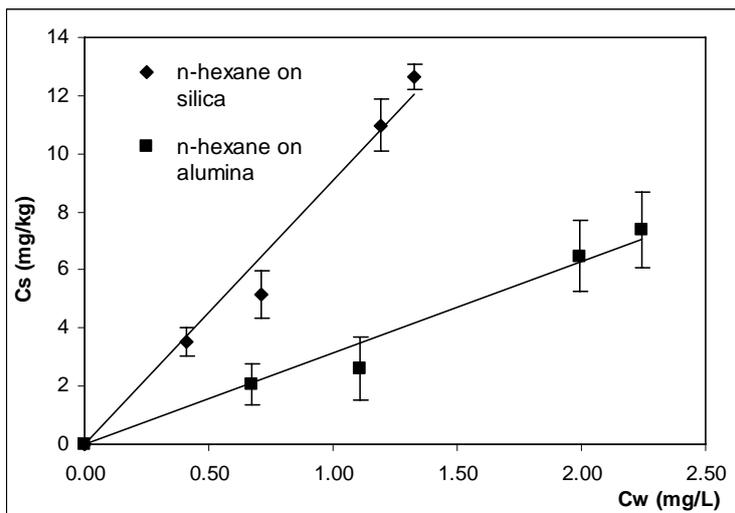


(a)

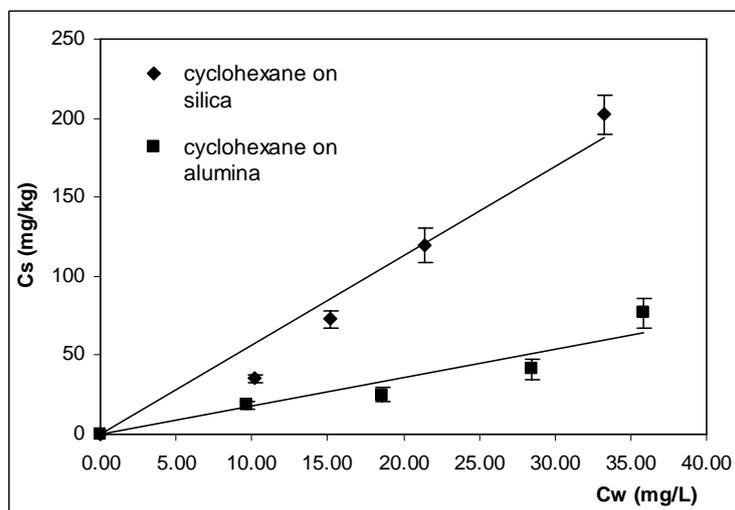


(b)

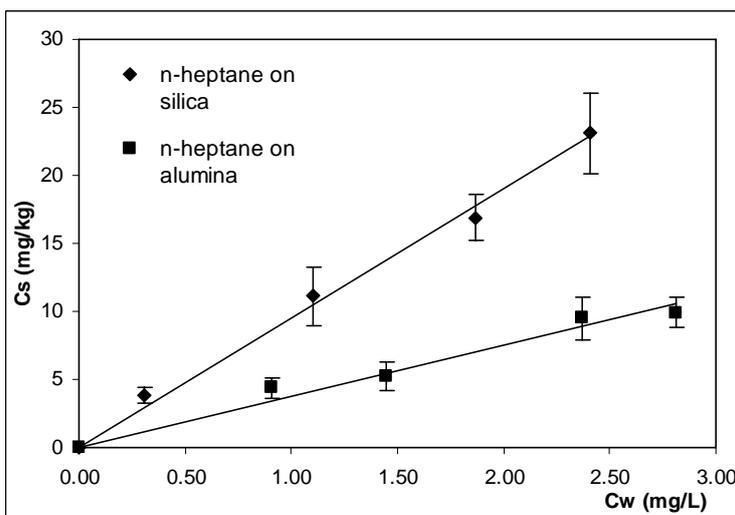
5. Characterizing the sorption mode by using alkane and cycloalkane



(c)

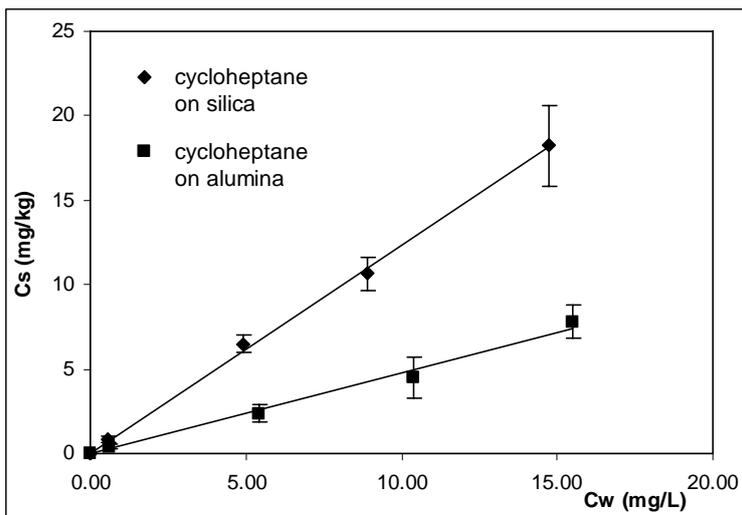


(d)

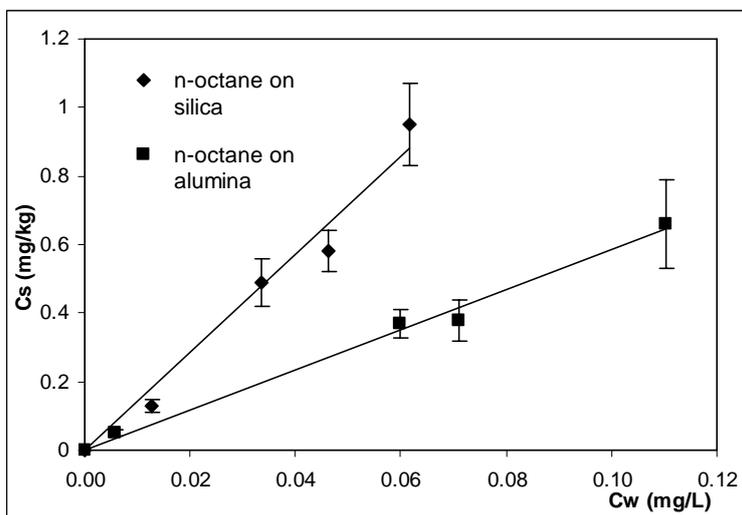


(e)

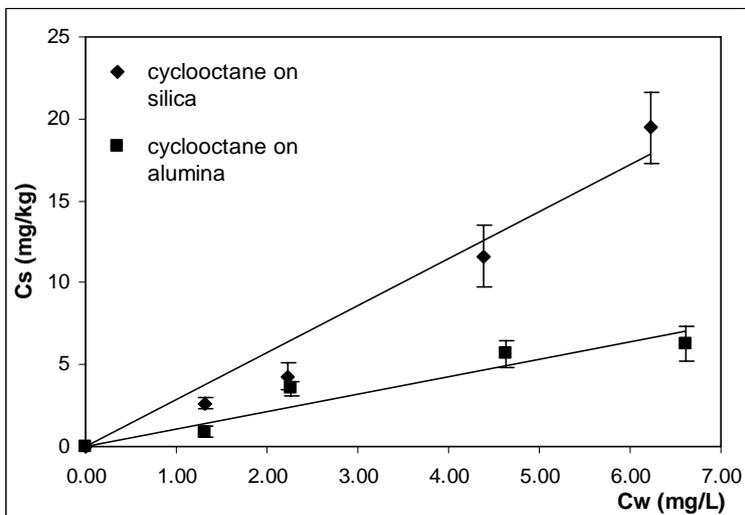
5. Characterizing the sorption mode by using alkane and cycloalkane



(f)



(g)



(h)

## 5. Characterizing the sorption mode by using alkane and cycloalkane

Fig.5-1 Sorption isotherms of selected n-alkanes and cycloalkanes on silica and alumina (at 25 °C, 0.005 M CaCl<sub>2</sub> as background electrolyte). (a) n-pentane, (b) cyclopentane, (c) n-hexane, (d) cyclohexane, (e) n-heptane, (f) cycloheptane, (g) n-octane, (h) cyclooctane.

**Table 5-2 determined sorption parameters of probe compounds on mineral surfaces**

Compound	Silica			Alumina		
	$K_d$ (L/kg) <sup>a</sup>	R <sup>2</sup>	$K_{dSA}$ (L/m <sup>2</sup> ) <sup>b</sup>	$K_d$ (L/kg) <sup>a</sup>	R <sup>2</sup>	$K_{dSA}$ (L/m <sup>2</sup> ) <sup>b</sup>
n-pentane	5.69 ± 1.06	0.958	1.31 ± 0.24 x 10 <sup>-5</sup>	1.73 ± 0.21	0.992	1.12 ± 0.14 x 10 <sup>-5</sup>
n-hexane	9.07 ± 1.01	0.981	2.09 ± 0.23 x 10 <sup>-5</sup>	3.16 ± 0.43	0.977	2.03 ± 0.28 x 10 <sup>-5</sup>
n-heptane	9.49 ± 1.46	0.994	2.18 ± 0.33 x 10 <sup>-5</sup>	3.69 ± 0.59	0.979	2.38 ± 0.38 x 10 <sup>-5</sup>
n-octane	14.31 ± 2.31	0.976	3.29 ± 0.53 x 10 <sup>-5</sup>	5.87 ± 1.41	0.993	3.78 ± 0.91 x 10 <sup>-5</sup>
cyclopentane	3.95 ± 0.79	0.960	0.91 ± 0.18 x 10 <sup>-5</sup>	0.98 ± 0.18	0.987	0.63 ± 0.12 x 10 <sup>-5</sup>
cyclohexane	5.66 ± 1.13	0.966	1.30 ± 0.26 x 10 <sup>-5</sup>	1.80 ± 0.38	0.905	1.16 ± 0.25 x 10 <sup>-5</sup>
cycloheptane	1.23 ± 0.17	0.998	0.28 ± 0.04 x 10 <sup>-5</sup>	0.48 ± 0.10	0.989	0.31 ± 0.06 x 10 <sup>-5</sup>
cyclooctane	2.86 ± 0.56	0.963	0.66 ± 0.13 x 10 <sup>-5</sup>	1.04 ± 0.38	0.916	0.67 ± 0.25 x 10 <sup>-5</sup>

a.  $K_d$  (L/kg) sorption coefficient based on the linear model (Eq. 5-3).

b.  $K_{dSA}$ , surface normalized sorption coefficient.

Background electrolyte: 0.005M CaCl<sub>2</sub>; error is defined as standard deviation

From the linear model based  $K_d$  values in Table 5-2, it was observed that the correlation of  $K_d$  (L/kg) values of n-alkanes to that of the water solubility  $S_w$  (mol/m<sup>3</sup>) on both investigated minerals was linear in logarithmic coordinates (Fig. 1):

$$\text{Silica : } \log K_d = 0.19 (-\log S_w) + 0.72 \quad (R^2 = 0.964) \quad (5-4)$$

$$\text{Aluminum oxide : } \log K_d = 0.25 (-\log S_w) + 0.23 \quad (R^2 = 0.984) \quad (5-5)$$

## 5. Characterizing the sorption mode by using alkane and cycloalkane

The similar slopes in equations (5-4) and (5-5) suggest that the mechanisms of sorption to these two mineral surfaces are the same. Furthermore, the distance about 0.5 log unit between two curves in Fig. 5-2 was caused by the surface area difference of ca 3. Such linear relationships have also been observed in our previous studies of sorption of polycyclic aromatic hydrocarbons to mineral surfaces (Qian et al., 2010).

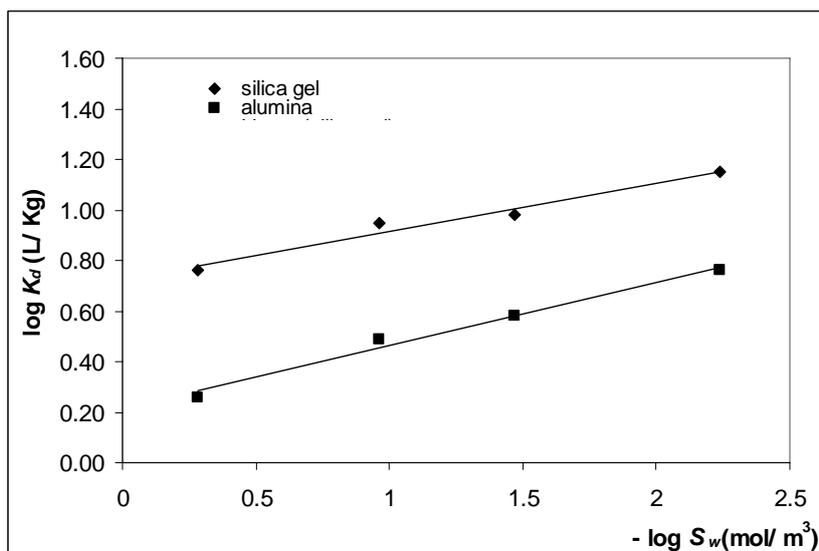


Fig.5-2 Relationship between  $\log K_d$  and  $\log S_w$  of n-alkanes on silica and aluminum oxide (at 25 °C)

In contrast, linear correlations were not found between  $\log K_d$  and  $\log S_w$  of cycloalkanes. The  $K_d$  values of cycloheptane and cyclooctane on both sorbents were unexpectedly small. The reason might be related to the molecular dimension, since cycloalkanes have larger dimensions than n-alkanes, thus the entrance of cycloalkanes into small pores on the sorbent could be limited.

### 5.3.2 $K_n/K_c$ ratio for sorption to water-mineral surfaces

Based on Equation (5-2),  $K_n/K_c$  ratios of four pairs of n- and cycloalkanes (linear model based  $K_d$  values listed in Table 5-2) were calculated and are listed in Table 5-3. The  $K_n/K_c$  ratios in both water-mineral systems were significantly lower than 1, between 0.13 and 0.35, which indicates that the dominating sorption mode to mineral surfaces in submerged

systems is absorption-like, requiring cavity formation. In contrast, the  $K_n/K_c$  ratios in air-mineral systems are above or close to 1 (Fig. 5-3), and sorption in air-mineral phase was recognized as adsorption.

**Table 5-3  $K_n/K_c$  ratios of alkanes (C5 to C8) in different water-mineral systems**

Number of carbon atoms	$K_n/K_c$ in water-silica	$K_n/K_c$ in water-alumina
5	0.22	0.27
6	0.23	0.25
7	0.33	0.35
8	0.14	0.15

However, comparison of the  $K_n/K_c$  ratios in water-mineral phases and in air-water phase (Fig. 5-3) shows that ratios in water-mineral phases are higher than those in air-water phase (governed only by absorption) (Plyasunov and Shock, 2000), which suggests that sorption in water-mineral phases probably can not be simply considered as pure absorption of organic compounds in a vicinal water phase near the mineral surface that shows different characteristics to the bulk water.

Su et al. proposed that in sorbent-water system, the water film on silica or alumina is considered to be only about one molecular-layer thick. The organic solute may adsorb more effectively than excess water by London forces on this water film (Su et al., 2006). Following this model, sorption of organic solute to the mono-water molecule layer should be considered as adsorption mode. Thus, in the vicinal water phase, a contribution of adsorption (on mono molecule water layer) might be relevant to the sorption process. If the model is true, it could be the reason why the  $K_n/K_c$  ratios in sorbent-water system are higher than that in sorbent-air system.

The lack of direct evidence of the distribution of solutes in the vicinal water phase currently hampers the understanding of the exact sorption mechanism. Further investigations to identify and characterize such near-surface aqueous zones are

fundamental for a more-indepth understanding of sorption processes at hydrophilic surfaces.

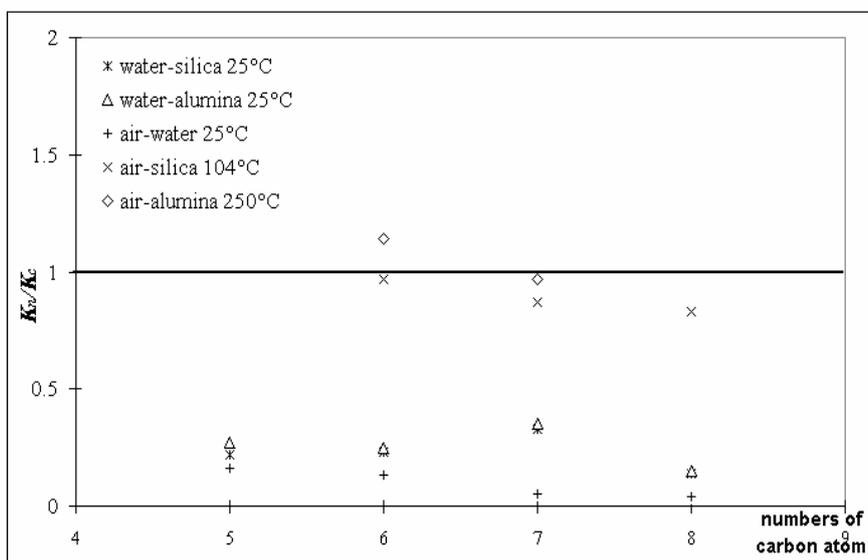


Fig.5-3  $K_n/K_c$  ratio in different systems (ratios in water-silica and water-alumina were obtained in this study, the other ratios were taken from Endo et al., 2008)

#### 5.4 Acknowledgements

Financial support for this work was provided by the Deutsche Forschungsgemeinschaft (DFG, grant SCHM2350/2-1). Special thanks go to Mrs. Claudia Schenk for the BET surface area determination. Thanks also to Christian Mayer for helpful discussions throughout this work.

#### 5.5 References

- Borisover, M. D., Graber, E. R., 1997, Specific interactions of organic compounds with soil organic carbon. *Chemosphere* 34, 1761–1776.
- Chiou, C. T., Peters, L. J., Freed, V. H., 1979, A physical concept of soil-water equilibriums for nonionic organic compounds. *Science* 206, 831-832

## 5. Characterizing the sorption mode by using alkane and cycloalkane

- Chiou, C. T., Porter, P. E., Schmedding, D. W., 1983, Partition equilibriums of nonionic organic compounds between soil organic matter and water. *Environ. Sci. Technol.* 17, 227-231.
- Delle Site, A., 2001, Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *J. Phys. Chem. Ref. Data.* 30, 187-439.
- Endo, S., Grathwohl, P., Schmidt, T.C., 2008, Absorption or Adsorption? Insights from molecular probes n-alkanes and cycloalkanes into modes of sorption by environmental solid matrices. *Environ. Sci. Technol.* 42, 3989-3995
- Endo, S., Grathwohl, P., Haderlein, S. B., Schmidt, T.C., 2009, Characterization of sorbent properties of soil organic matter and carbonaceous geosorbents using n-alkanes and cycloalkanes as molecular probes. *Environ. Sci. Technol.* 43, 193-400
- Endo, S., Grathwohl, P., Haderlein, S. B., Schmidt, T.C., 2009, Supporting information for “Characterization of sorbent properties of soil organic matter and carbonaceous geosorbents using n-alkanes and cycloalkanes as molecular probes.” freely available via <http://pubs.acs.org>
- Goss, K.-U., Schwarzenbach, R. P., 2001, Linear free energy relationships used to evaluate equilibrium partitioning of organic compounds. *Environ. Sci. Technol.* 35, 1–9
- Goss, K.-U., 2004, Comment on “Influence of soot carbon on the soilair partitioning of polycyclic aromatic hydrocarbon”. *Environ. Sci. Technol.* 38, 1622–1623.
- Goss, K.-U., Bronner, G., 2006, What is so special about the sorption behavior of highly fluorinated compounds? *J. Phys. Chem. A*, 110, 9518-9522
- Huang, W., Schlautman, M. A., Weber, W. J. Jr., 1996, A distributed reactivity model for sorption by soils and sediments. 5. The influence of near-surface characteristics in mineral domains. *Environ. Sci. Technol.* 30, 2993-3000
- Mader, B. T., Goss, K.-U., Eisenreich, S. J., 1997, Sorption of nonionic, hydrophobic organic chemicals to mineral surfaces. *Environ. Sci. Technol.* 31, 1079-1086
- Müller, S., Totsche, K. U.; Kögel-Knabner, I., 2007, Sorption of polycyclic aromatic hydrocabons to mineral surfaces. *Eur. J. Soil Sci.* 58, 918-931

## 5. Characterizing the sorption mode by using alkane and cycloalkane

- Piatt, J. J., Backhus, D. A., Capel, P. D., Eisenreich, S. J., 1996, Temperature-dependent sorption of naphthalene, phenanthrene and pyrene to low organic carbon aquifer sediments. *Environ. Sci. Technol.* 30, 751-760.
- Plyasunov, A. V., Shock, E. L. 2000, Thermodynamic functions of hydration of hydrocarbons at 298.15 K and 0.1 MPa. *Geochim. Cosmochim. Acta* 64, 439–468.
- Qian, Y., Bi, E., Bakkour, R., Schmidt, T. C., 2010, Sorption of polycyclic aromatic hydrocarbons (PAHs) on minerals surfaces in aqueous solution: an HPLC type column study. *Water Res.* submitted
- Roth, C. M., Goss, K.-U., Schwarzenbach, R. P., 2005a, Sorption of a diverse set of organic vapors to diesel soot and road tunnel aerosols. *Environ. Sci. Technol.* 39, 6632-6637
- Roth, C. M., Goss, K.-U., Schwarzenbach, R. P., 2005b, Sorption of a diverse set of organic vapors to urban aerosols. *Environ. Sci. Technol.* 39, 6638-6643
- Schwarzenbach, R. P., Westall, J. C., 1981, Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. *Environ. Sci. Technol.* 15, 1360-1367.
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2003. Environmental Organic Chemistry, 2nd Ed., Wiley, New York,
- Su, Y. H., Zhu, Y. G., Sheng, G., Chiou, C. T., 2006, Linear adsorption of nonionic organic compounds from water on to hydrophilic minerals : silica and alumina. *Environ. Sci. Technol.* 40, 6949-6954

## 6. Characterization of sorption mechanism in near-surface zone on hydrophilic surfaces using scanning electrochemical microscopy (SECM)

### 6.1 Introduction

Sorption of PAHs on the hydrophilic inorganic surface leads to the accumulation of PAHs near or on the surface and causes the concentrations of PAHs in so called near-surface zone higher than in the bulk phase, thus a concentration gradient in such zone formed. As mentioned in previous chapters, two potential mechanisms, *absorption* and *adsorption*, are considered to explain the sorption of PAHs to mineral surfaces. According to the concept of these two modes, adsorption requires that the PAH molecules replace the water molecules and adhere in the layer (monolayer) just out of the mineral surfaces, while by absorption the PAH molecules accumulate in the “vicinal water layer” (Mader et al., 1997, Chiou, 2002, Schwarzenbach et al., 2003). Following both modes, adsorption indicates the thickness of near-surface zone is in the range of only one or maximal several PAHs molecules; absorption suggests the thickness could extend to the range of sub-micrometer. Therefore, instrumental methods that can observe concentration gradients and thickness of near-surface zone would strongly improve the understanding of sorption mechanisms.

In order to identify such a gradient, a suitable tool for highly spatially resolved analysis of compounds in the sub-micrometer range is essential. A novel electrochemical method with the capability of measurements at very high spatial resolution is scanning electrochemical microscopy (SECM). It is a very flexible tool, which qualifies it for a wide variety of surface analyses and modifications (Bard and Mirkin, 2001; Turcu et al., 2004; Ufheil et al., 2005). The set-up of a typical SECM is shown in Figure 6-1. It contains an ultramicroelectrode (UME), which is controlled by a 3-axis position controller with movement step in micrometer or sub-micrometer range, a reference electrode (RE) and a counter electrode (CE). Like other scanning probe techniques, SECM is based on the possibility of precisely positioning a probe close to the object under investigation. In the case of SECM, the probe is an ultramicroelectrode, which is an electrode of nanometer to micrometer dimension. UME and substrate are both immersed into an electrolyte solution containing either an oxidizable or reducible chemical species. The UME is electrically biased so that a redox current, the tip-current, is generated. When the UME is brought near the substrate the tip-current changes and information about the surface reactivity of the

substrate can be extracted. By scanning the UME laterally above the substrate one can acquire an image of its topography and/or its surface reactivity (Schröck et al., 2005).

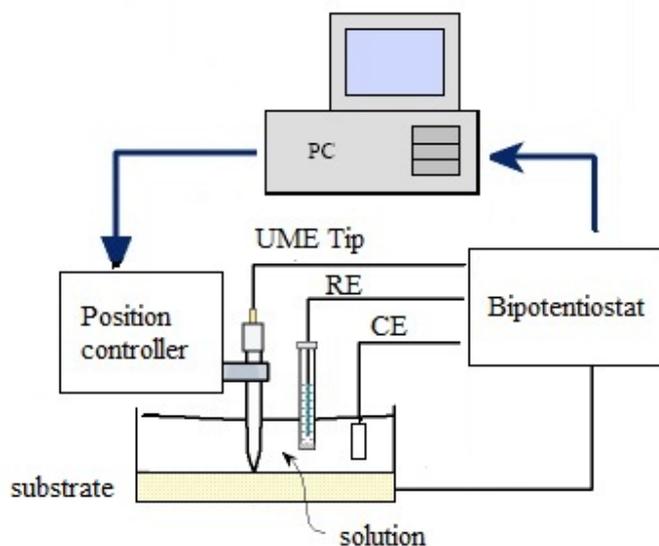


Figure 6-1 Schematic SECM set-up (adapted from Koester (2000))

Based on the precisely movable tips of ultramicroelectrodes, SECM provides highly spatially resolved electrochemical measurements. The developed ultramicroelectrode can demonstrate the application of the SECM technique in the nanometer range.

## 6.2 Materials

Two PAHs, phenanthrene and pyrene were selected as probe compounds. Calcium chloride, phenanthrene and pyrene were purchased from Sigma-Aldrich. Phenanthrene and pyrene were recrystallized in analytical grade ethanol and dried prior to use. The purity of calcium chloride was above 99% and used without further purification. PAH stock solutions were prepared in methanol at varying concentrations, and all solutions were diluted with Milli-Q grade water (Resistance >18 M $\Omega$ ) and stored in dark under ambient condition.

Three kinds of glass were chosen as sorbents, indium-tin-oxide coated glass (ITO glass, Sensolytics GmbH, Bochum, Germany), normal microscope slides (VWR, Germany) and chlorotrimethylsilane coated microscope slides (home-made).

### 6.3 Methods

#### 6.3.1 Sorption on ITO glass

The most commonly used method in SECM is the amperometric feedback mode, which requires that the surface should be conductive and the compounds have very fast redox activities. Unfortunately, our glass surfaces of interest are insulators. Thus, an alternative material, an indium-tin-oxide coated glass (ITO glass) was used in the first investigation. Indium tin oxide is a solid solution of indium (III) oxide ( $\text{In}_2\text{O}_3$ ) and tin (IV) oxide ( $\text{SnO}_2$ ), typically 90%  $\text{In}_2\text{O}_3$ , 10%  $\text{SnO}_2$  by weight. The ITO glass has an electrically conductive surface.

Since the PAHs are not redox-active compounds, the potential or current can not be directly measured in the classic SECM application. However, the determination of conductivity after adding certain ions to the aqueous solutions is possible. In previous experiments, we found that in the presence of cation (such as  $\text{Ca}^{2+}$ ), sorption coefficients of PAHs ( $K_d$ ) on glass surfaces increased. Zhu et al. (2004) proposed that this phenomenon was caused by so called cation- $\pi$  bonding. The glass surface has a negative charge and the PAH molecule is also partly negative charged due to the  $\pi$  bonding.  $\text{Ca}^{2+}$  can be located in between and form sandwich like complexes. If their hypothesis is true, due to cation- $\pi$  bonding the concentration of  $\text{Ca}^{2+}$  in the near-surface zone should also be higher than that in the bulk phase. Thus the conductivity measured between the UME tip and the ITO glass surface should decrease with increasing distance. Based on this concept, the experiments were carried out to measure the change of conductivity at different distances. A 25  $\mu\text{m}$  electrode (Sensolytics GmbH, Bochum, Germany) equipped SECM (Sensolytics GmbH, Bochum, Germany) was used in the study. The experimental setup is shown in Fig. 6-2.

The experimental procedure was:

1. Fill freshly prepared  $\text{CaCl}_2$  solution with interested concentration 1 mL in the container, manually set the UME tip attaching the ITO surface, then adjust it at a position 1  $\mu\text{m}$  away

from the surface by using the position controller, measure the conductivity. Move the tip up with constant step, measure conductivity at each depth until the tip at 1000  $\mu\text{m}$  away from the surface. Afterwards, move the tip towards surface with same internal distance; record the conductivity again at each depth.

2. Add PAH solution (with varying concentrations) 1mL into  $\text{CaCl}_2$  solution; wait for 30 min. Again set the UME tip attaching the ITO surface, then adjust it 1  $\mu\text{m}$  away from the surface, follow procedure 1, measure conductivity at different depth up to a distance of 1000  $\mu\text{m}$ . Move the tip completely out of the solution, wait another 30 min. Reset the tip at the position 1000  $\mu\text{m}$  away from the surface, move the tip towards the surface with same internal distance and measure conductivity at each depth.

All measurements were carried out in triplicates.

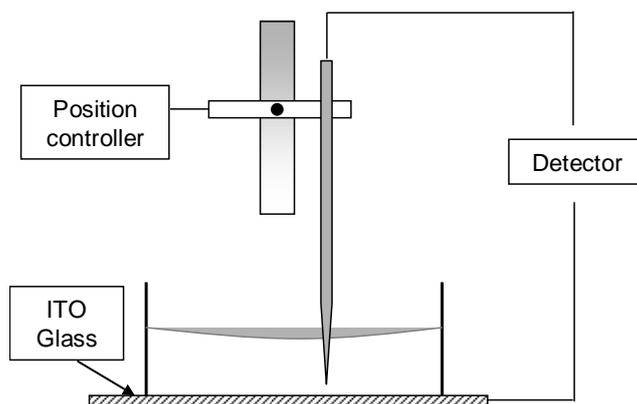


Fig. 6-2 Experimental configuration for determination of sorption on ITO glass

### 6.3.2 Sorption on nonconductive glass

For further development, the concentration gradient of PAHs on the nonconductive glass surface (e.g. normal glass and silane coated glass) was considered to be measured by using two position fixed electrodes system (Fig. 6-3). The conductivity between two electrodes is generally depending on the concentration of  $\text{CaCl}_2$  at each depth. If a concentration gradient caused by sorption is formed, through cation- $\pi$  bonding the conductivity at different depth should also vary. However, in this method, the measured conductivity between the two fixed electrodes is strongly depending on the conductive surface area of

the electrodes (e.g. the radius of electrode). Due to limit of the sensitivity, the 1 mm electrodes (home-made) had to be used in the investigations.

The experimental procedure was the same as described in 6.3.1. All experiments were measured in triplicates.

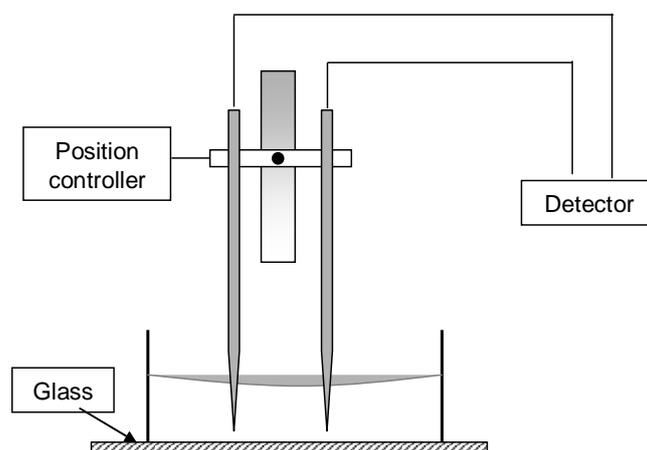


Fig. 6-3 Experimental configuration for determination of sorption on glass

## 6.4 Results and discussions

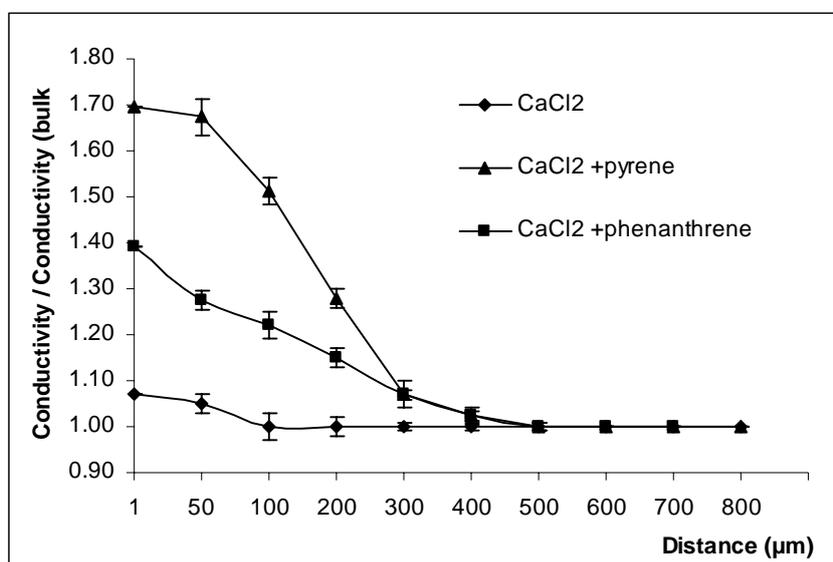
### 6.4.1 Sorption on ITO glass

Generally, the conductivity measured at 1000  $\mu\text{m}$  away from the all investigated surface was found no difference to the conductivity measured in the bulk and thus considered as the conductivity in bulk, which was recorded as “conductivity (bulk)”.

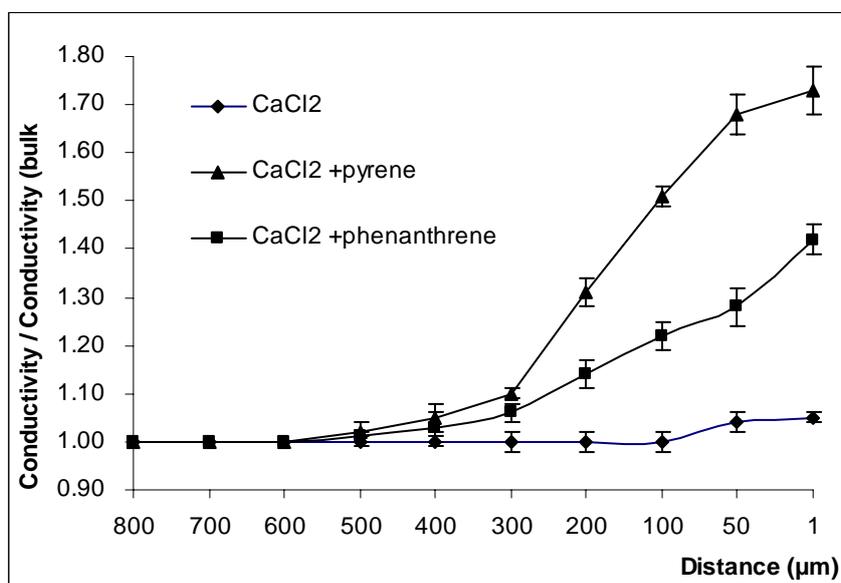
The measured changes of conductivity on ITO glass are plotted in Fig. 6-4. When the ITO glass was submerged in pure  $\text{CaCl}_2$  solution, the conductivity did not change with increasing distance between electrode and ITO glass surface. This indicated that the  $\text{CaCl}_2$  solution was homogenous. After adding phenanthrene or pyrene into the  $\text{CaCl}_2$  solutions, the conductivity decreased with increasing distance. This phenomenon suggests that the concentration of  $\text{CaCl}_2$  near the surface was higher than that in the bulk phase. Further, it fits the hypothesis, that accumulation of PAHs near the surface influenced the distribution of Calcium cation through the cation- $\pi$  bonding effect. The results also showed

reversibility (no hysteresis was found in two opposite direction movements, see Fig. 6-4 (a) and (b)).

Furthermore, our measured conductivity showed that the thickness of concentration gradient layer is about 300  $\mu\text{m}$ . This distance is certainly beyond the electrical double layer, which is typically in the range of several hundred nanometers (Hamann et al., 2007). Therefore, the concentration gradient of  $\text{CaCl}_2$  was considered as the result of sorption of PAHs to the glass surfaces, which might be able to represent the concentration gradient of PAHs formed due to the accumulation of PAHs in the near-surface zone.



(a)



(b)

Fig. 6-4 decrease of the conductivity vs. distance between electrode tip and ITO surface (concentration of  $\text{CaCl}_2$ , phenanthrene and pyrene are 1 mol/L, 75  $\mu\text{g/L}$  and 50  $\mu\text{g/L}$ , respectively) (a) UME tip away from surface; (b) UME tip towards surface

#### 6.4.2 Sorption on nonconductive glass

##### Sorption on normal glass

The relative changes of conductivity versus distance away from normal glass surface were plotted in Fig. 6-5. Results showed the same trend as the achieved on ITO glass. The conductivity between two UME tips was kept constant in only  $\text{CaCl}_2$  solution at different depth. After adding PAH (e.g. phenanthrene or pyrene) in the  $\text{CaCl}_2$  solution, the conductivity was observed to decrease significantly with increasing the distance between 1 to 300  $\mu\text{m}$ . Similar to the sorption on ITO glass, the change of conductivities showed also no hysteresis in two opposite direction movements. Furthermore, the decrease in conductivity follows the order pyrene > phenanthrene. This may also indicate sorption of pyrene to glass is stronger than phenanthrene, which was also concluded in chapter 3.

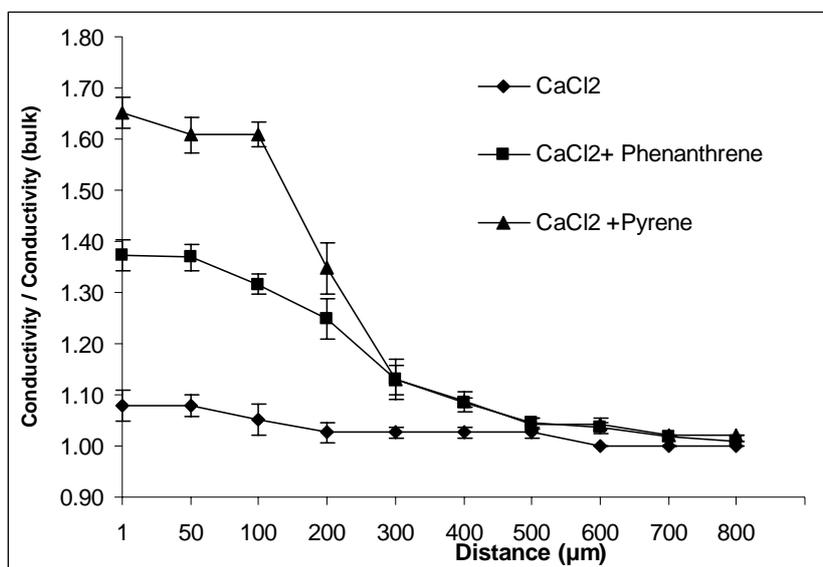


Fig. 6-5 decrease of the conductivity vs. distance between electrode tip and glass surface (concentration of  $\text{CaCl}_2$ , phenanthrene and pyrene are 1 mol/L, 75  $\mu\text{g/L}$  and 50  $\mu\text{g/L}$  respectively)

To identify the relationship between decrease in conductivity and the concentration of pyrene, three different concentrations of pyrene were used in the further studies (keep concentration of  $\text{CaCl}_2$  at 1 mol/L). The measured results are presented in Fig 6-6. As shown in Fig. 6-6, the decrease of conductivity has no dependency on the concentration of pyrene added into the  $\text{CaCl}_2$  solution.

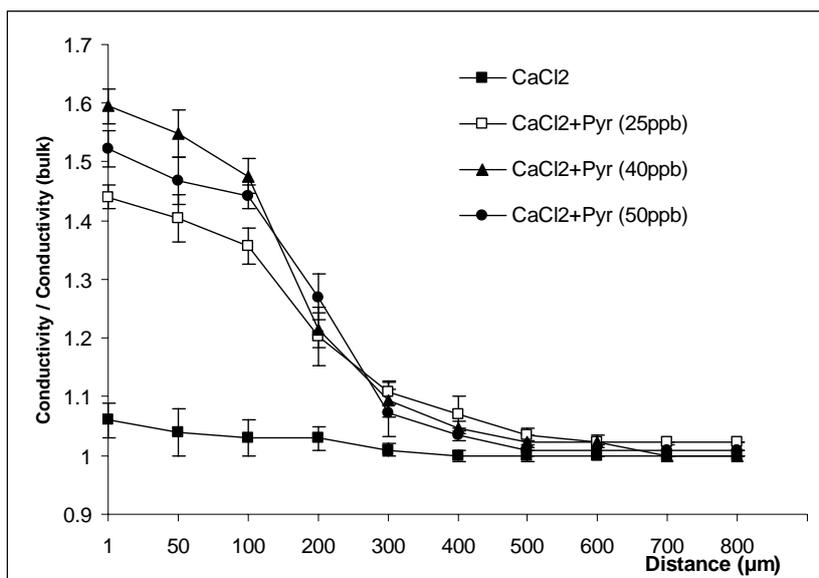


Fig 6-6 decrease of conductivity vs. distance with different concentration of pyrene (concentration of  $\text{CaCl}_2$  is 1 mol/L) on glass surface

The effect of ionic strength has been investigated using different concentrations of  $\text{CaCl}_2$  (0.1 mol/L, 1 mol/L and 5 mol/L), the concentration of pyrene in the solution was kept at 50  $\mu\text{g/L}$ . The obtained curve of decrease of conductivity vs. distance at concentration of  $\text{CaCl}_2$  5 mol/L showed the same trend as that obtained at concentration of  $\text{CaCl}_2$  1 mol/L (Fig. 6-5, the curve of  $\text{CaCl}_2$  + pyrene). Due to limit of sensitivity, the conductivity was not able to be measured in solution with concentration of  $\text{CaCl}_2$  at 0.1 mol/L.

In all current investigations, the data indicated again the 300  $\mu\text{m}$  thick zone is a relevant region for characterizing the sorption mechanism of PAHs on glass surface. Such zone on hydrophilic surfaces was also reported by Zheng et al., (2006). The thickness of the zone in their study was even found in the extension to 600  $\mu\text{m}$  away from the surface. However, the exact mechanism in such zone could not be explained.

### Sorption on silane coated glass

In chapter 3, sorption coefficient of pyrene to the silane coated glass was found significantly decreased. Thus, the silane coated glass was used instead of normal glass in the further SECM investigations. The measured changes of conductivity vs. distance away from surface were plotted in Fig. 6-7. The results showed that concentration gradient had been formed in only  $\text{CaCl}_2$  contained solution. The concentration gradient region is located from 300 to 500  $\mu\text{m}$  away to the surface. After adding pyrene, the changes of conductivity were found more intensive. However, the concentration gradient region had not been changed, which did not indicate whether sorption occurred or not. More detailed investigations needs to be done in the future.

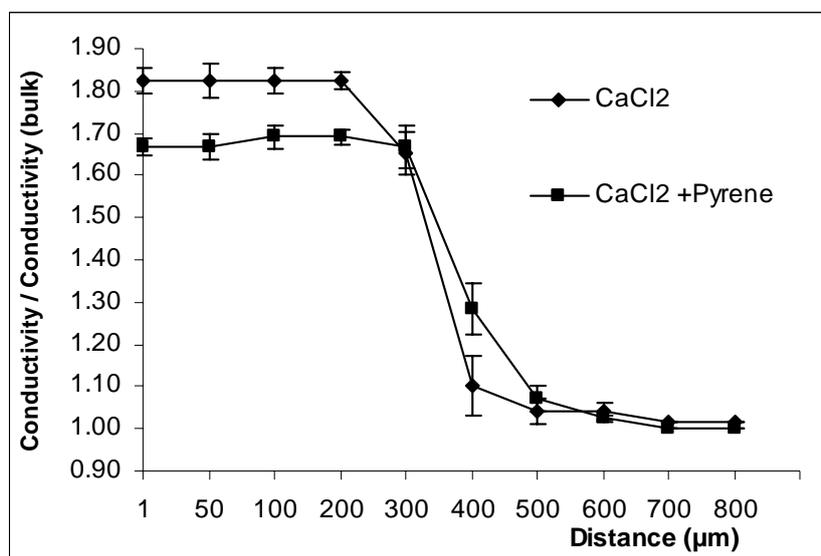


Fig. 6-7 decrease of the conductivity vs. distance between electrode tip and silane coated glass surface (concentration of  $\text{CaCl}_2$  and pyrene are 1 mol/L and 50  $\mu\text{g/L}$ , respectively)

SECM has already proven a powerful tool for study of sorption phenomena and characterization of the near-surface aqueous zone. The application and utilization of this method in current research is just a very preliminary work. SECM surely will give rise to further insights in the water structure along mineral surfaces.

### 6.5 Reference

- Chiou, C. T., 2002, Partition and adsorption of organic contaminants in environmental systems. John Wiley & Sons.
- Bard, A. J., Mirkin, M. V., 2001, Scanning Electrochemical Microscopy. Marcel Dekker Inc. New York,
- Hamann, C. H., Hamnett, A. and Vielstich, W., 2007, Electrochemistry, 2nd Ed. Wiley-VCH: Weinheim
- Koester, O., 2000, Ein Beitrag zur Elektrochemischen Sensorik: Entwicklung und Charakterisierung von planaren amperometrischen Mikroelektroden unter Einsatz statischer und dynamischer Testverfahren. Dissertation, University of Duisburg
- Mader, B. T., Goss, K.-U., Eisenreich, S. J., 1997, Sorption of nonionic, hydrophobic organic chemicals to mineral surfaces. *Environ. Sci. Technol.* 31, 1079-1086
- Turcu, F., Schulte, A., Schuhmann, W., 2004, Scanning electrochemical microscopy (SECM) of nanolitre droplets using an integrated working/reference electrode assembly. *Anal. Bioanal. Chem.* 380, 736-741.
- Schröck, K., Schulte, A., Schuhmann, W., 2005, Visualization of the reaction zones between two miscible solutions with potentiometric and amperometric microsensors. *Electroanal.* 17, 489-494.
- Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M., 2003. Environmental organic chemistry. 2nd Ed., Wiley: New York.
- Ufheil, J., Heß, C., Borgwarth, K., Heinze, J., 2005, Nanostructuring and nanoanalysis by scanning electrochemical microscopy (SECM). *Phys. Chem. Chem. Phys.* 7, 3185-3190.
- Zheng, J., Chin, W.-C., Khijniak, E., Khijniak, E., Jr., Pollack, G. H., 2006, Surface and interfacial water: Evidence that hydrophilic surfaces have long-range impact. *Adv. Colloid Interface Sci.* 127, 19-27
- Zhu, D. Q., Herbert, B. E., Schlautman, M. A., Carraway, E. R., Hur, J., 2004, Cation- $\pi$  bonding: A new perspective on the sorption of polycyclic aromatic hydrocarbons to mineral surfaces. *J. Environ. Qual.* 33, 1322-1330.

## **7. General conclusions and outlook**

### **7.1 General Conclusions**

The HPLC type column chromatography is proven a suitable and reliable tool to determine the sorption of hydrophobic organic compounds (especial polycyclic aromatic hydrocarbons, PAHs) on hydrophilic inorganic surfaces by comparing the measures sorption coefficient to the corresponding batch results and the literature data.

A linear relationship between sorption coefficients  $K_d$  and the subcooled water solubility  $S_w$  of investigated PAHs in logarithmic coordinates on all investigated minerals (borosilicate glass, silica gel, aluminum oxide and titanium oxide) was observed. This relationship could help to predict  $K_d$  values of other PAHs.

On borosilicate glass, sorption of PAHs was found difficult to suppress. Our results indicate that the mass loss of PAHs caused by sorption is closely related to the sorption coefficient  $K_d$  and the ratio of solution volume to contacted surface area (V/S). If a mass loss of  $w$  % is tolerated, the V/S ratio needs to be larger than  $(100/w - 1) \times K_d$ . This formula offers a useful tool for analysts to estimate the necessity of the correction.

On porous material, the  $K_d$  values obtained from various surface areas did not show a correlation to the surface area, which indicates the effective surface area in aqueous conditions is not equivalent to BET-N<sub>2</sub> determined surface area under dry conditions.

By using the ratio of  $K_n/K_c$ , the results suggested that sorption in the water-inorganic surfaces system was dominated by absorption in the vicinal water layer.

The concentration gradient in the near-surface zone was represented by measuring the change of conductivity in ionic solutions using SECM. The conductivity was observed to decrease significantly with increasing distance between 1 to 300  $\mu\text{m}$ . Such thickness of the concentration gradient layer suggests also the sorption mode of PAHs on glass surface is likely absorption in the extensional water layer.

### **7.2 Outlook**

The developed HPLC type column chromatography showed some advantages (such as less time consuming than batch approach, easily simulate the environmental conditions) and

could in theory be used for determination of the sorption coefficients of a wide variety of compounds (e.g. PCBs, other priority contaminants) to the environmental solids, especially on borosilicate glass, which is often used in environmental analysis.

For sorption of HOCs on the porous materials in aqueous, the effective surface area in aqueous solution is a very important parameter. Therefore how to measure and define the effective surface area in aqueous solution is a critical issue in the water-sorbent system.

The SECM has been successfully applied into the study of sorption processes to hydrophilic surfaces. However, the investigations carried out in this project are just some fundamental work. To achieve a meaningful explanation of sorption mechanisms, a series of further investigations need to be done: (1) use monovalent and trivalent cations instead of bivalent cation; (2) use redox-active cations, such as  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , thus a commonly applied method in SECM system, the amperometric feedback mode can be introduced into studies. (3) change the distance between two position fixed electrodes (see chapter 6, Fig. 6-3 ).

## 8. Appendixes

Table 1 Packed columns with inorganic materials

Column (material)	L * ID (mm)	particle size ( $\mu\text{m}$ )	surface area ( $\text{m}^2/\text{g}$ )	Porosity	Bulk density ( $\text{g}/\text{cm}^3$ )
Glass beads (Bischoff)	53 * 3	30	1.05	0.350	1.73
Silica gel (Merck)	53 * 3	63-100	435	0.757	0.53
Silica gel (Bischoff)	53 * 3	10	300	0.792	0.46
Aluminum oxide (Bischoff)	53 * 3	10	116	0.715	1.00
Titanium dioxide 60 (Sachtleben)	53 * 3	10	96.7	0.688	1.22
Titanium dioxide 300 (Sachtleben)	53 * 3	10	19.7	0.640	1.40

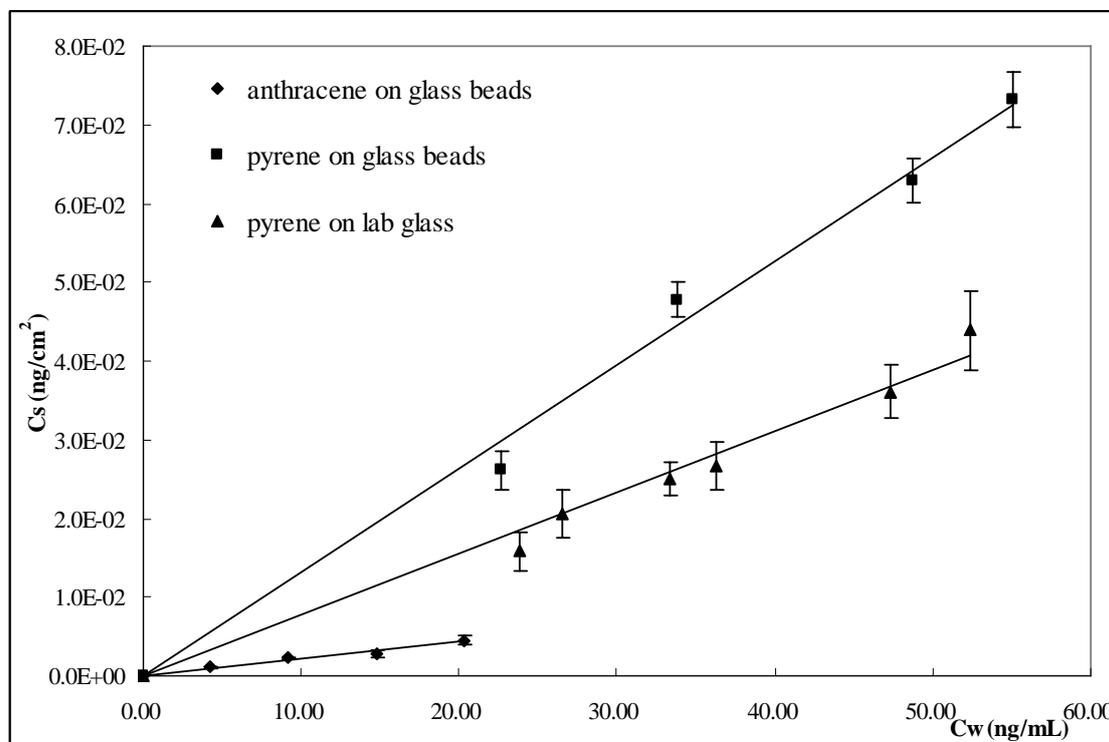


Fig. 1 sorption isotherms of anthracene and pyrene on different glass surface in batch experiment in chapter 3 (Table3-2)

**Table 2 determined retardation factors of PAHs on glass surfaces at varied conditions  
(corresponding to chapter 3)**

Conditions		Retardation factors				
Mobile phase	Temp. (°C)	NAP	FLU	ANT	PHE	PYR
0.005 M CaCl <sub>2</sub>	25	1.30	4.31	12.27	11.53	48.01
0.005 M CaCl <sub>2</sub>	15	-	4.95	14.69	11.97	50.48
0.005 M CaCl <sub>2</sub>	40	-	4.26	11.92	10.09	44.20
Milli-Q water	25	1.18	4.17	10.97	8.99	30.42
0.001 M CaCl <sub>2</sub>	25	-	-	-	10.44	42.82
0.05 M CaCl <sub>2</sub>	25	-	-	-	10.89	46.87
0.1 M CaCl <sub>2</sub>	25	-	-	-	11.23	47.86
pH =3 solution	25	-	-	-	9.85	39.65
pH=5 solution	25	-	-	-	9.54	34.48
pH=8 solution	25	-	-	-	9.31	33.82

**Table 3 determined retardation factors of PAHs on different minerals (corresponding to chapter 4, Table 4-2)**

Conditions		Retardation factor ( $R_f$ )				
Sorbents	Temp. (°C)	NAP	FLU	ANT	PHE	PYR
Silica gel (Merck)	25	1.47	3.41	8.98	6.76	25.57
Alumina	25	1.17	3.39	9.20	6.34	26.74
Titanium dioxide 60	25	1.12	2.05	7.08	5.20	19.26

0.005 M CaCl<sub>2</sub> solution was used as mobile phase

**Table 4 determined retardation factors of PAHs on silica gel (Merck) at varied conditions (corresponding to chapter 4)**

Conditions		Retardation factor ( $R_f$ )		
Mobile phase	Temperature (°C)	ANT	PHE	PYR
0.005 M CaCl <sub>2</sub>	25	8.98	6.76	25.57
0.005 M CaCl <sub>2</sub>	15	10.42	7.13	27.14
0.005 M CaCl <sub>2</sub>	40	8.27	6.07	23.28
Milli-Q water	25	-	6.50	20.59
0.05 M CaCl <sub>2</sub>	25	-	7.03	26.29
0.1 M CaCl <sub>2</sub>	25	-	6.99	26.01
pH =3 solution	25	-	6.29	21.73
pH=8 solution	25	-	6.57	22.36

**Table 5 determined retardation factors of PAHs on alumina at varied conditions  
(corresponding to chapter 4)**

Conditions		Retardation factor ( $R_f$ )	
Mobile phase	Temp. (°C)	PHE	PYR
0.005 M CaCl <sub>2</sub>	25	6.34	26.74
0.005 M CaCl <sub>2</sub>	15	-	30.52
0.005 M CaCl <sub>2</sub>	40	-	23.99
Milli-Q water	25	6.30	24.96
0.05 M CaCl <sub>2</sub>	25	6.47	28.65
0.1 M CaCl <sub>2</sub>	25	6.50	28.09
pH =5 solution	25	6.01	24.93
pH=8 solution	25	6.36	25.14

**Table 6 determined retardation factors of PAHs on titanium dioxide 60 at varied conditions  
(corresponding to chapter 4)**

Conditions		Retardation factor ( $R_f$ )	
Mobile phase	Temp. (°C)	PHE	PYR
0.005 M CaCl <sub>2</sub>	25	5.20	19.26
0.005 M CaCl <sub>2</sub>	15	-	20.74
0.005 M CaCl <sub>2</sub>	40	-	17.81
Milli-Q water	25	5.24	19.94
0.05 M CaCl <sub>2</sub>	25	5.27	19.62
0.1 M CaCl <sub>2</sub>	25	5.10	19.65
pH =5 solution	25	4.94	19.10
pH=8 solution	25	5.34	20.65

**Table 7 determined the changes of conductivity on the ITO glass surface (corresponding to chapter 6, Fig 6-4)**

Distance ( $\mu\text{m}$ )	Conductivity / Conductivity (bulk)		
	CaCl <sub>2</sub>	CaCl <sub>2</sub> + PHE	CaCl <sub>2</sub> + PYR
1	1.07	1.39	1.70
50	1.05	1.27	1.67
100	1.00	1.22	1.51
200	1.00	1.15	1.28
300	1.00	1.07	1.07
400	1.00	1.02	1.02
500	1.00	1.00	1.00
600	1.00	1.00	1.00
700	1.00	1.00	1.00
800	1.00	1.00	1.00
conductivity (bulk)	0.013 mS	0.039 mS	0.043 mS

Concentration of CaCl<sub>2</sub>, phenanthrene and pyrene are 1 mol/L, 75  $\mu\text{g/L}$  and 50  $\mu\text{g/L}$ , respectively; 25  $\mu\text{m}$  electrode.

**Table 8 determined the changes of conductivity on the normal glass surface (corresponding to chapter 6, Fig 6-5)**

Distance ( $\mu\text{m}$ )	Conductivity / Conductivity (bulk)		
	$\text{CaCl}_2$	$\text{CaCl}_2 + \text{PHE}$	$\text{CaCl}_2 + \text{PYR}$
1	1.08	1.37	1.65
50	1.08	1.37	1.61
100	1.05	1.32	1.61
200	1.03	1.25	1.35
300	1.03	1.13	1.13
400	1.03	1.08	1.09
500	1.03	1.04	1.04
600	1.00	1.04	1.02
700	1.00	1.02	1.01
800	1.00	1.01	1.00
conductivity (bulk)	0.037 $\mu\text{S}$	0.022 $\mu\text{S}$	0.023 $\mu\text{S}$

Concentration of  $\text{CaCl}_2$ , phenanthrene and pyrene are 1 mol/L, 75  $\mu\text{g/L}$  and 50  $\mu\text{g/L}$ , respectively; 1 mm electrode.

**Table 9 determined the changes of conductivity on the silane coated glass surface  
(corresponding to chapter 6, Fig 6-7)**

Distance ( $\mu\text{m}$ )	Conductivity / Conductivity (bulk)	
	CaCl <sub>2</sub>	CaCl <sub>2</sub> + PYR
1	1.83	1.67
50	1.83	1.67
100	1.83	1.69
200	1.83	1.69
300	1.65	1.67
400	1.10	1.29
500	1.04	1.07
600	1.04	1.02
700	1.01	1.00
800	1.01	1.00
conductivity (bulk)	0.035 $\mu\text{S}$	0.042 $\mu\text{S}$

Concentration of CaCl<sub>2</sub>, phenanthrene and pyrene are 1 mol/L, 75  $\mu\text{g/L}$  and 50  $\mu\text{g/L}$ , respectively; 1 mm electrode.



The CV is not included in the online version, for reasons of data protection.

## Publication List

### Articles

Qian, Y., Posch, T., Schmidt, T. C., Sorption of polycyclic aromatic hydrocarbons (PAHs) on glass surfaces. *Chemosphere* (2010), doi:10.1016/j.chemosphere.2010.11.002

Li, B., Qian, Y., Bi, E., Chen, K., Schmidt, T.C., Sorption behavior of phthalic acid esters on reference soils evaluated by soil column chromatography, *CLEAN – Soil, Air, Water*, 2010, 38, 425–429

Qian, Y., Bi, E., Bakkour, R., Schmidt, T. C., Evaluating the sorption of polycyclic aromatic hydrocarbons (PAHs) on minerals surfaces: An HPLC type column study. *Water Res.* 2010, submitted

### Posters and presentations

Qian, Y., Schmidt, T. C., An HPLC-based approach to evaluate adsorption of hydrophobic organic compounds (HOCs) on inorganic surfaces in aqueous solution. *27<sup>th</sup> International Symposium on Chromatography*. 2008, Muenster, Germany

Qian, Y., Schmidt, T. C., Adsorption of hydrophobic organic compounds (HOCs) on inorganic surface in aqueous systems. *The 25<sup>th</sup> Annual International Conference on Soils, Sediments, Water and Energy*. 2009, Amherst, USA

Qian, Y., Schmidt, T. C., Adsorption of hydrophobic organic compounds to inorganic surfaces in aqueous solution. *Wasser 2008*, Jahrestagung der Wasserchemischen Gesellschaft. Trier, Germany

Qian, Y., Altergott, O., Schmidt, T. C., Evaluation of the adsorption of hydrophobic organic compounds (HOCs) to inorganic surfaces in aqueous solution by using batch and column method. *Wasser 2009*, Jahrestagung der Wasserchemischen Gesellschaft. Stralsund, Germany

Qian, Y., Posch, T., Jung, L. Schmidt, T. C., Characterizing the sorption mode to mineral surfaces in aqueous solution by using alkane and cycloalkane probe compounds. *Wasser 2010*, Jahrestagung der Wasserchemischen Gesellschaft. Bayreuth, Germany

## **DECLARATION**

Hereby, I declare that all the results and data included in this dissertation were obtained from my independent work. All sources and auxiliary materials used by me in this dissertation were cited completely.

Essen,